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Annual Report

on Grant No. NAG-1-419-2

A STUDY OF THE APPLICABILITY OF NUCLEAT ON THEORY TO QUASI-THERMODYNAMIC TRANSITIONS OF SECOND AND HIGHER EHRENFEST-ORDER

Submitted to:

National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia 23665

Attention: Dr. Noel T. Wakelyn (Project Manager)
MD M/S 226B

Submitted by:

R. E. Barker, Jr.
Professor

K. W. Campbell
Research Assistant

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July 1985

SCHOOL OF ENGINEERING AND APPLIED SCIENCE

DEPARTMENT OF MATERIALS SCIENCE

UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VIRGINIA 22901

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FOREWORD

The research reported herein was performed in the Materials Science Department of the University of Virginia, Charlottesville, Virginia 22901. The work was initiated under grant number NASA-NAG-1-419, "A Study of the Applicability of Nucleation Theory to Quasi-Thermodynamic Transitions of Second and Higher Ehrenfest-Order." This report covers research performed from December 1983 to December 1984. Since the major portion of the first year's work involved the theoretical development of a relatively unexplored area the results of these efforts are presented in a more detailed fashion than usual in this Annual Report. The investigators for this project are Dr. R. Edward Barker, Jr., principal investigator, and Kenny W. Campbell, graduate research assistant.

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SECTION I

ABSTRACT

The applicability of classical nucleation theory to second (and higher) order thermodynamic transitions in the Ehrenfest sense has been investigated and expressions have been derived upon which the qualitative and quantitative success of the basic approach must ultimately depend. The expressions describe the effect of temperature undercooling, hydrostatic pressure, and tensile stress upon the critical parameters, the critical nucleus size, and critical free energy barrier, for nucleation in a thermodynamic transition of any general order. These expressions are then specialized for the case of first and second order transitions. The expressions for the case of undercooling are then used in conjunction with literature data to estimate values for the critical quantities in a system undergoing a pseudo-second order transition (the glass transition in polystyrene). Methods of estimating the interfacial energy γ in systems undergoing a first and second order transition are also discussed. Plans for future research and a list of publications and presentations accompanied by manuscripts and abstracts are also included.

SECTION II

INTRODUCTION

A. General Background

As in the case of so many other important concepts in science, the foundations of nucleation theory were laid a century ago by Gibbs.[1] Important developments which put the subject of homogeneous nucleation in a form recognizable by modern students occurred in the 1920's and 1930's when Volmer and Weber[2] and Becker and Doring[3] sought to understand the phenomenon of vapor condensation. Subsequently the concepts of heterogeneous nucleation were developed, so that modern nucleation theory includes both homogeneous and heterogeneous models.

The theory has been applied to phase transformations in metals and to a large extent metallurgists have tended to dominate in the major developments in the field for many years. Nevertheless, some significant specialized applications of nucleation theory have been made by polymer scientists. Among the most notable are the efforts by Price[4], Hoffman and Lauritzen[5], Lindenmeyer[6], and others to understand the originally unexpected lamellar morphology of polymer single crystals and the kinetics of chain folding in such crystals.

Nucleation theory has previously been successfully applied only to thermodynamic transitions of first order in the Ehrenfest sense. However, in this work, classical nucleation theory is applied to transitions of second (and higher) order.

B. Meaning and Significance of a Second Order Transition

In the Ehrenfest classification of phase transitions, the order of a given transition is determined by which derivatives of the Gibbs free

energy are discontinuous. Thus, in the present thermodynamic context, the phrase "second order" refers to physical processes of a fundamental nature and not necessarily to correction factors of small magnitude. According to the definition, a second order phrase transition in the Ehrenfest sense is one in which the Gibbs free energy and its first derivatives are continuous at the transition point while the second derivatives are discontinuous. The primary discontinuous properties associated with the second derivatives are changes in the thermal expansivity $\Delta\alpha$, the isothermal compressibility $\Delta\beta$, and the heat capacity at constant pressure ΔC_p. Hence, a second order phase transition is characterized by "jumps" in such thermodynamic quantities as those mentioned above and thus differ from a first order transition only in the quantities which exhibit discontinuity and not in fundamental significance as thermodynamic phase transition.

C. The Thermodynamic Basis of Nucleation Theory

As is widely known, when a pure system of molecules (atoms included) which exists as an equilibrium (stable) phase α at a given set of intensive variables (T_1, ρ_1, etc.), is subjected to new intensive conditions (T_2, ρ_2, etc.) where α is no longer the only stable phase but where one or more new phases are stable, then it is possible that the expected transformation

$$\alpha \rightarrow \beta \qquad (1)$$

will occur only slowly, if at all, within a finite observation period. According to the precepts of nucleation theory, the reason for this inhibition of the expected transformation is that molecular fluctuations and diffusive motion must occur which create a small particle of β within the α-milieu (but see ref. 7) and that there is an interface between the

α and β regions in which the molecules have an excess free energy $\gamma = \gamma_{\alpha\beta}$ per unit area. Thus the true Gibbs free energy change corresponding to the transformation of a small amount of α into a small nucleus of β is not merely the so-called bulk thermodynamic value ΔG (energy per mole); it is instead

$$\Delta G = V_\beta(\Delta G/\upsilon_\beta) + A_{\alpha\beta}\gamma_{\alpha\beta} \qquad (2)$$

where V_β is the volume of the β-nucleus, υ_β is the molar volume, and $A_{\alpha\beta}$ is the interfacial area of β. If the growing nucleus has more than one type of interface, then the term $A_{\alpha\beta}\gamma_{\alpha\beta}$ would imply a summation over the relevant areas.

Thus, according to nucleation theory local density fluctuations will lead to the formation of a small nucleus of β-phase within an α-phase matrix if the temperature is less than the normal transition temperature T_t° for $\alpha \underset{\leftarrow}{\rightarrow}$ where β is the stable phase when $T < T_t^\circ$ (Fig. 1). The total interfacial energy $A_{\alpha\beta}\gamma_{\alpha\beta}$ will oppose the enlargement of the nucleus, and a bulk free energy gV_β will encourage growth (Fig. 2). The term

$$g \equiv (G_\beta - G_\alpha)/\upsilon_\beta \qquad (3)$$

represents the free energy change per unit volume of transformed material. Equation (2) now becomes

$$\Delta G = gV_\beta + \gamma A_\beta \ . \qquad (4)$$

D. The Customary Approximations

In the standard treatments, $\Delta G = \Delta H - T\Delta S$ is approximated, at a degree of under cooling

$$\theta = T_t^\circ - T \qquad (5)$$

by $\Delta H \approx \Delta H_t^\circ$, $\Delta S \approx \Delta H_t^\circ/T_t^\circ$ which may be seen to give

$$\Delta G \simeq \Delta S_t^\circ \cdot \theta \text{ where } \Delta S_t^\circ \simeq \frac{\Delta H_t^\circ}{T_t^\circ} \qquad (6)$$

or

$$g = s_t \theta \text{ with } s_t = \Delta S_t^\circ / v_\beta . \qquad (7)$$

The standard treatments next proceded by taking $\partial(\Delta G)/\partial r = 0$, where r is the radius of a spherical nucleus for which

$$V_\beta = (4/3)\pi r^3 \text{ and } A_\beta = 4\pi r^2 \quad . \qquad (8)$$

This gives the size of the critical nucleus r_c to be

$$r_c \simeq -2\gamma/g \ . \qquad (9)$$

For the stable $\alpha \rightarrow \beta$ transition, g will be negative (g = 0 for the equilibrium transition). Substitution of Eq. (9) back into Eq. (4) gives the usual type of expression for the "activation barrier" that must be overcome before the continued growth of the β-nucleus can take place.

$$\Delta G_c = (16\pi/3)\gamma^3/g^2 \simeq 16.76\ \gamma^3/g^2 \ . \qquad (10)$$

This barrier, and the critical size r_c, are of course both dependent on the degree of under cooling, through Eq. (7), therefore

$$r_c = -2\gamma/s_t\theta \simeq \frac{-2\gamma(T_t^\circ/\theta)}{h^\circ} \text{ and } \Delta G_c = \left(\frac{16\pi}{3}\right) \gamma^3/s_t^2\theta^2 \ . \qquad (11)$$

SECTION III

SUMMARY OF PROGRESS, PAPERS AND PRESENTATIONS

A. Summary of Progress on Research Grant NASA-NAG-1-419

The main idea behind the basis for our work is that if we break away from the conventional approximation that leads to Eqs. (6) and (7), instead introducing the assumption that ΔG and therefore g can be expanded as a Taylor series in θ, to which Maxwell's relations and some other thermodynamic operations are subsequently applied, then we have a powerful, relatively simple, and (as far as we have been able to ascertain) a previously undiscovered formalism for predicting (1) non-linear correction terms for first order thermodynamic transitions, (2) the size and barrier height for second order transitions (in the Ehrenfest sense), and (3) the possibility of a formal extension of nucleation theory to even higher order transitions. Since the new theory brings in the higher order effects as analytic thermodynamic terms (rather than merely mathematical or empirical approximations) it is a more flexible theory for predicting other effects, such as the influence of changes in pressure, stress, electric field, etc. The new theory, for the same reason, should also be more amenable to the incorporation of ideas from statistical mechanics; and to compositional and kinetic extensions such as Couchman's [8] T_g theory and the time-temperature transformation concepts of Enns and Gillham [9].

1. Expansion in Terms of Undercooling.

The initial situation to which the formalism described above is applied is a system which is temperature undercooled below a normal (STP) transition point.

(a) Central features of the new approach.

As outlined in the previous section it is possible to construct a useful, and apparently overlooked, formalism by what in its barest form is the expedient of expanding the effective free energy of the transformed nucleus in a Maclaurin series in θ (the degree of undercooling), and then utilizing thermodynamical relations to evaluate the expansion coefficients. For example, if we take

$$g = g(\theta) = g(0) + g'(0)\theta + (1/2)g''(0)\theta^2 + \ldots \tag{12}$$

$$= a_0 + a_1\theta + a_2\theta^2 \ldots \tag{13}$$

then $g'(0)$, which means $(\partial g/\partial\theta)_p$ at $\theta = 0$, can be found as follows,

$$\left(\frac{\partial g}{\partial \theta}\right)_p = \left(\frac{\partial g}{\partial T}\right)_p \left(\frac{\partial T}{\partial \theta}\right)_p = -\left(\frac{\partial g}{\partial T}\right)_p , \tag{14}$$

but

$$G_\beta - G_\alpha = H_\beta - H_\alpha - T(S_\beta - S_\alpha), \tag{15}$$

so that

$$g \equiv (G_\beta - G_\alpha)/v_\beta = h - Ts, \tag{16}$$

where

$$h \equiv (H_\beta - H_\alpha)/v_\beta \text{ and } s \equiv (S_\beta - S_\alpha)/v_\beta. \tag{17}$$

Carrying through the operations required,

$$\left(\frac{\partial g}{\partial T}\right)_p = \frac{1}{v_\beta}\left[\left(\frac{\partial G_\beta}{\partial T}\right)_p - \left(\frac{\partial G_\alpha}{\partial T}\right)_p\right]$$

$$- \frac{1}{v_\beta^2}(G_\beta - G_\alpha)\left(\frac{\partial v_\beta}{\partial T}\right)_p \tag{18}$$

$$= -\frac{1}{v_\beta}(S_\beta - S_\alpha) - g\alpha_\beta, \tag{19}$$

where use has been made of the thermodynamic relations $S = -(\partial G/\partial T)_p$ and thermal expansivity $= \alpha = (\partial v/\partial T)_p/v$.

(b) Calculations of the coefficients.

Further reduction of Eq. (18) gives

$$\left(\frac{\partial g}{\partial T}\right)_p = -\frac{h}{T} - g\left(\frac{\partial \alpha_\beta}{\partial T}\right)_p , \tag{20}$$

and thus, using Eq. (13) at $T = T_t$, or $\theta = 0$, we obtain

$$a_1 = g'(0) \equiv \left(\frac{\partial g}{\partial \theta}\right)_p \Bigg|_{\theta=0} = +\frac{h_t}{T_t} , \tag{21}$$

because $g(0)$ is zero (when $T = T_t$). In a similar fashion, it can be shown that

$$g''(\theta) = -\frac{1}{v_\beta}\left(\frac{\partial S_\beta}{\partial T} - \frac{\partial S_\alpha}{\partial T}\right)_p + \frac{\alpha_\beta}{v_\beta}(S_\beta - S_\alpha)$$

$$-\alpha_\beta \left(\frac{\partial g}{\partial T}\right)_p - g\left(\frac{\partial \alpha_\beta}{\partial T}\right)_p . \tag{22}$$

After some reduction, Eq. (22) evaluated at $\theta = 0$ gives

$$g''(0) = -\frac{(C_p)_\beta - (C_p)_\alpha}{v_\beta T_t} + \frac{2\alpha_\beta h_t}{T_t} . \tag{23}$$

An examination of Eqs. (12)-(23) reveals that

$$a_o = 0, \; a_1 = h/T_t,$$
$$a_2 = -(\Delta C_p/2v_\beta h_t) + (\alpha_\beta h_t/T_t), \; \ldots \tag{24}$$

(c) Results.

The results obtained through the series expansion will now be discussed. These results will be interpreted for both first and second order Ehrenfest transitions. These mathamatical results will

then be used to give semiquantitative results for both classes of transitions in representative systems.

First order transitions:

A revisitation of Eq. (9) with the incorporation of the expansion derived in the previous sections gives a critical nucleus

$$r_c = -2\gamma/g = -2\gamma/(a_1\theta + a_2\theta^2 + \ldots), \tag{25}$$

$$r_c = -\frac{2\gamma(T_t/\theta)}{h_t}\,\frac{1}{1 - [(\Delta C_p/2\nu_\beta h_t) - \alpha_\beta]\,\theta + \ldots}, \tag{26}$$

where h_t is a negative number for an exothermic transition.

Similarly, incorporation of Eq. (10) with the expanded results gives an activation energy barrier

$$\Delta G_c = (16\pi/3)\gamma^3/g^2 = (16\pi/3)\gamma^3/(a_1\theta + a_2\theta^2 + \ldots)^2, \tag{27}$$

$$\Delta G_c = \frac{(16\pi/3)\gamma^3(T_t/\theta)^2}{(h_t)^2} \cdot \frac{1}{1 - [(\Delta C_p/2\nu_\beta h_t) - \alpha_\beta]^2\theta^2 + \ldots}. \tag{28}$$

These equations reduce to the conventional expressions given in Eq. (11) when the higher-order correction terms are neglected. Thus as a result of the expansion of the free energy in a Taylor series, we have explicit, convenient, and (in principle) experimentally accessible correction factors for first order homogeneous nucleation theory.

Second-order transitions:

In a second-order Ehrenfest transition, since the latent heat is zero, the conventional expressions given in Eq. (11) are physically meaningless because in both cases the denominator is zero. However, using the results derived in the preceeding section for r_c and ΔG_c,

meaningful results for the critical nucleus size and critical activation energy for second order transitions can be determined. Thus evaluating Eq. (26) for the case where $h_t = 0$ gives a critical nucleus

$$r_c = \frac{4\gamma v_\beta T_t}{(\Delta C_p)\theta^2} \quad . \tag{29}$$

Similarly, evaluating Eq. (28) for the case where $h_t = 0$ gives an activation energy barrier

$$\Delta G_c = \frac{(64\pi/3)\gamma^3 v_\beta^2 T_t}{(\Delta C_p)^2 \theta^4} \quad . \tag{30}$$

There is evidence that the interfacial energy $\gamma = \gamma_{\alpha\beta}$ between phases separated by a second order transition may have a zero value at the equilibrium second order transition temperature.[10] However on the basis of our continuing investigation we suspect that at a degree of undercooling $\theta = T - T_t$, which is the point of concern in the present argument, γ will not vanish because the curves for the total surface energies $\gamma(\alpha)$ and $\gamma(\beta)$ have different slopes $\partial\gamma(\alpha)/\partial T$ and $\partial\gamma(\beta)/\partial T$ (Fig. 3). In the case of the glass transition in polymers where $T_t = T_g$, α corresponds to the rubbery (liquid) state and β to the glassy state. The underlying physical phenomenon is the existence of molecular fluctuation which give rise to the formation of a small embryo.

Hence a mathematical formulation for applying classical nucleation theory to second order Ehrenfest transitions is found through the expansion of the Gibbs free energy in a Maclaurin series.

(d) Numerical results for undercooled systems.

A semiquantitative graphical representation of the results is given in Figs. 4-9 using typical data for the first order liquid to solid transition of water and the quasi-second order glass transition of polystyrene. In Fig. 4 and Fig. 5 the critical parameters for a first order transition are plotted against the degree of supercooling using both the conventional and expanded approaches. These plots serve to give an order of magnitude estimation as to the size of the "correction factor" discussed earlier. Figure 6 shows a relationship similar to the qualitative representation of Fig. 2 in which the free energy is plotted against the cluster size for various degrees of supercooling. The peak of each curve gives the values for r_c and G_c. The values of the data were collected from various sources in the literature and are listed in Refs. 11 and 12.

Figures 7 and 8 graphically show the size of the critical parameters as a function of assumed interfacial energy between the glassy and rubbery states of polystyrene at a fifty degree supercooling. The use of an assumed interfacial energy is a consequence of the lack of data of this type in the literature. The values chosen, although somewhat arbitrary, are believed to be of the proper magnitude for such systems. Figure 9 shows the variation of the critical nucleus size with the assumed interfacial energy for various degrees of supercooling. The source of the data plotted for polystyrene is given in Refs. 13 and 14.

As indicated above, appropriate experimental data for the interfacial energy $\gamma_{\alpha\beta} = \gamma$ are not presently available. Therefore we

have chosen γ as an independent variable for graphical representation in Figs. 7, 8, and 9. Current research efforts are directed toward the determination of appropriate values of γ. These plots serve to provide guides for the design of relevant experiments to measure this interfacial energy.

2. Expansion in Terms of Applied Hydrostatic Pressure.

The formalism developed earlier and applied in the previous section will now be utilized to predict the effects of an applied hydrostatic pressure.

(a) Predicted effects of hydrostatic pressure.

As outlined earlier, the main point of the theory is the expansion of the free energy in a Maclaurin series.

This expansion in terms of $\Delta P = P - P_o$, where P_o is the initial pressure of the system, may be expressed as follows

$$g = g(\Delta P) = g(0) + g'(0)\Delta P + \tfrac{1}{2}g''(0)(\Delta P)^2 + \ldots \qquad (31)$$

$$= b_o + b_1\Delta P + b_2(\Delta P)^2 + \ldots \qquad (32)$$

where, for example, $b_1 = g'(0) = (\partial g/\partial P)_T$ evaluated at $\Delta P = 0$. It should be noted that g is also a function of temperature and thus g evaluated at $\Delta P = 0$ is not necessarily zero unless the function is also evaluated at the normal temperature for the transition at the initial pressure of the system. Alternately stated, the function is also evaluated at a degree of supercooling θ equaling zero as in BC-I.[15] Thus for example a system which is initially at atmospheric pressure (P_o = 1 atm.), g(0) equals zero when the function is evaluated both at $P = P_o$ or $\Delta P = 0$ and at the normal transition temperature $T = T_t^o$ or θ

= 0. Since this is the case in the present discussion, $b_o = g(0)$ in Eq. (32) will be zero.

From the definition $g = \Delta G/v_\beta$ and relations such as $v_\alpha = (\partial G_\alpha/\partial P)_T$, and $\beta_\alpha = -(\partial \ln v_\alpha/\partial P)_T$ for the volume and compressibility of the α-phase, it follows that

$$g'(0) \equiv \left(\frac{\partial g}{\partial \Delta P}\right)_T = \left(\frac{\partial g}{\partial P}\right)_T = \frac{1}{v_\beta}\left[\left(\frac{\partial G_\beta}{\partial P}\right)_T - \left(\frac{\partial G_\alpha}{\partial P}\right)_T\right] - \left[\left(\frac{G_\beta - G_\alpha}{v_\beta^2}\right)\left(\frac{\partial v_\beta}{\partial P}\right)_T\right]\Bigg|_{\Delta P=0} \tag{33}$$

Thus at $\Delta P = 0$ and $\theta = 0$ we have

$$g'(0) = b_1 = \frac{v_\beta - v_\alpha}{v_\beta} = \frac{\Delta v}{v_\beta} \tag{34}$$

where $\Delta v = v_\beta - v_\alpha$. Note that $G_\beta - G_\alpha$ in Eq. (33) is zero for the reasons discussed previously.

In a similar way,

$$g''(0) = \frac{1}{v_\beta}\left[\left(\frac{\partial v_\beta}{\partial P}\right)_T - \left(\frac{\partial v_\alpha}{\partial P}\right)_T\right] - \frac{1}{v_\beta^2}\left[(v_\beta - v_\alpha)\left(\frac{\partial v_\beta}{\partial P}\right)_T\right] + \left[g\left(\frac{\partial \beta_\beta}{\partial P}\right)_T + \left(\frac{\partial g}{\partial P}\right)_T \beta_\beta\right]\Bigg|_{\Delta P=0} \tag{35}$$

After reduction and evaluation at $\Delta P = 0$ and $\theta = 0$

$$\tfrac{1}{2}g''(0) = b_2 = \tfrac{1}{2}\left[\frac{v_\alpha}{v_\beta}(\beta_\alpha - \beta_\beta) + \frac{(v_\beta - v_\alpha)\beta_\beta}{v_\beta}\right] \tag{36}$$

Summarizing the results of the expansion

$$g(0) = b_o = \frac{\Delta G}{v_\beta}\Big|_{\Delta P=0} = 0 \tag{37}$$

$$g'(0) = b_1 = \frac{v_\beta - v_\alpha}{v_\beta} = \frac{\Delta v}{v_\beta} \tag{38}$$

$$b_2 = \tfrac{1}{2}\left(-\frac{v_\alpha}{v_\beta}\Delta\beta + \frac{\beta_\beta}{v_\beta}\Delta v\right) \tag{39}$$

(b) Results for a first-order transition.

Use can now be made of Eqs. (9) and (10) by incorporating the results of the free energy expansion to obtain expressions for the critical nucleus size and critical energy barrier for a first order transition occurring isothermally under the influence of an applied pressure. The critical nucleus size is found from Eq. (9) to be

$$r_c = 2\gamma/g = -2\gamma/(b_o + b_1\Delta P + b_2(\Delta P)^2 + \ldots) \tag{40}$$

$$r_c \simeq \frac{-2\gamma}{\frac{\Delta v}{v_\beta}\Delta P - \left[\frac{1}{2}\left(\frac{v_\alpha}{v_\beta}\Delta\beta - \frac{\beta_\beta}{v_\beta}\Delta v\right)\right](\Delta P)^2 + \ldots} \tag{41}$$

Similarly the critical energy barrier is found to be

$$\Delta G_c = \frac{(16\pi/3)\gamma^3}{\left[\frac{\Delta v}{v_\beta}\Delta P - \tfrac{1}{2}\left(\frac{v_\alpha}{v_\beta}\Delta\beta - \frac{\beta_\beta}{v_\beta}\Delta v\right)(\Delta P)^2\right]^2} \tag{42}$$

Thus relatively simple expressions have been found for r_c and ΔG_c for phase transitions induced by the application of pressure.

(c) Results for second-order transitions.

As in the previous section, expressions for r_c and ΔG_c can be found for second-order transitions which occur in the presence of an applied pressure. For a second-order transition

$$v_\alpha = v_\beta \quad \text{or} \quad \Delta v = 0 \tag{43}$$

so that the value of g reduces to

$$-\tfrac{1}{2}\Delta\beta(\Delta P)^2 \tag{44}$$

Therefore the theoretical value of r_c in a second-order transition, induced by applied pressure, is found to be

$$r_c \simeq \frac{4\gamma}{\Delta\beta(\Delta P)^2} \tag{45}$$

Similarly, the theoretical value for the critical energy barrier is

$$\Delta G_c \simeq \frac{(64\pi/3)\gamma^3}{(\Delta\beta)^2(\Delta P)^4} \tag{46}$$

3. Expansion in Terms of Applied Tensile Stress.

The new approach will next be applied to the case of an applied tensile stress.

(a) Mathematical development in terms of stress.

The same type of derivation which was carried out for the case of applied pressure will now be developed for the application of a tensile stress. Although very similar in some respects to the previous case, there are some important differences which require a rather detailed presentation, rather than merely treating the stress as a negative pressure. Starting in the same way as for Eq. (31) we have

$$g = g(\sigma) = g(0)+g'(0)\sigma+\tfrac{1}{2}g''(0)\sigma^2+ \ldots \tag{47}$$

$$= b'_0 + b'_1\,\sigma + b'_2\,\sigma^2 + \ldots \tag{48}$$

where $\sigma = F/A_o$ is the nominal stress and $g'(o)$ denotes $(\partial g/\partial\sigma)_{P,T}$ at $\sigma = 0$. This derivative can be expressed as follows

$$\left(\frac{\partial g}{\partial \sigma}\right)_{P,T} = \left(\frac{\partial g}{\partial F}\right)_{P,T}\left(\frac{\partial F}{\partial \sigma}\right)_{P,T} = A_o\left(\frac{\partial g}{\partial F}\right)_{P,T} \tag{49}$$

where A_o is the initial cross-sectional area.

Carrying through the required operations

$$g'(0) \equiv \left(\frac{\partial g}{\partial \sigma}\right)_{P,T} = A\left(\frac{\partial g}{\partial F}\right)_{P,T} = A\left\{\frac{1}{v_\beta}\left[\left(\frac{\partial G_\beta}{\partial F}\right)_{P,T} - \left(\frac{\partial G_\alpha}{\partial F}\right)_{P,T}\right] - \left[\left(\frac{G_\beta - G_\alpha}{v_\beta^2}\right)\left(\frac{\partial v_\beta}{\partial F}\right)_{P,T}\right]\right\}\Bigg|_{\sigma=0} \quad (50)$$

Use will now be made of the thermodynamic relation $(\partial G/\partial F)_{P,T} = -L$. Thus at $\sigma = 0$ or $F = 0$ we have

$$g'(0) = b_1' = A\left[\frac{-(L_\beta - L_\alpha)}{v_\beta}\right] = \frac{-\Delta L}{v_\beta} \quad A \quad (51)$$

where $\Delta L = L_\beta - L_\alpha$ and $g(0)$ is zero when $\sigma = 0$ or $F = 0$.

In a similar fashion, it can be shown that

$$g''(0) = \left(\frac{\partial^2 g}{\partial F^2}\right)A^2\Big|_{\sigma=0} = A^2\left\{\frac{1}{v_\beta}\left[\left(\frac{\partial L_\alpha}{\partial F}\right)_{P,T} - \left(\frac{\partial L_\beta}{\partial F}\right)_{P,T}\right] - \left[\frac{(L_\alpha - L_\beta)}{v_\beta^2}\left(\frac{\partial v_\beta}{\partial F}\right)_{P,T}\right]\right.$$

$$\left. - \left[\frac{v_\beta\left(\frac{\partial g}{\partial F}\right)_{P,T} - g\left(\frac{\partial v_\beta}{\partial F}\right)_{P,T}}{v_\beta^2}\right]\left(\frac{\partial v_\beta}{\partial F}\right)_{P,T} + \left[\left(\frac{g}{v_\beta}\right)\left(\frac{\partial^2 v_\beta}{\partial F^2}\right)_{P,T}\right]\right\}_{\sigma=0} \quad (52)$$

After reduction, Eq (52) evaluated at $\sigma = 0$ gives

$$\tfrac{1}{2}g''(0) = b_2' = \left\{\frac{1}{2v_\beta}\left[\left(\frac{L}{YA}\right)_\alpha - \left(\frac{L}{YA}\right)_\beta\right] + \left[\left(\frac{\Delta L}{v_\beta^2}\right)\left(\frac{\partial v_\beta}{\partial F}\right)_{P,T}\right]\right\}A^2 \quad (53)$$

where use has been made of the relation $(\partial L/\partial F) = L/YA_o$ where Y is the Young's modulus.

Collecting the resulting coefficients,

$$g(0) = b_o' = \frac{\Delta G}{v_\beta}\Big|_{\sigma=0} = 0 \quad (54)$$

$$g'(0) = b_1' = A\left|\frac{-(L_\beta - L_\alpha)}{v_\beta}\right| = \frac{-\Delta L}{v_\beta}A \tag{55}$$

$$\tfrac{1}{2}g''(0) = b_2' = \left\{\frac{1}{2v_\beta}\left[\left(\frac{L}{YA}\right)_\alpha - \left(\frac{L}{YA}\right)_\beta\right] + \left[\left(\frac{\Delta L}{v_\beta}\right)\left(\frac{\partial v_\beta}{\partial F}\right)_{P,T}\right]\right\}A^2 \tag{56}$$

(b) Results for a first order transition.

Following the procedure outlined previously for the case of applied pressure, one can find the expressions for r_c and ΔG_c for the case of applied stress.

$$r_c = -2\gamma/g = -2\gamma/(b'_o + b'_1\sigma + b'_2\sigma^2 + \ldots) \tag{57}$$

$$r_c = \frac{-2\gamma}{-\left(\frac{\Delta LA\sigma}{v_\beta}\right) + \left\{\frac{1}{2v_\beta}\left[\left(\frac{L}{YA}\right)_\alpha - \left(\frac{L}{YA}\right)_\beta\right] + \left[\frac{\Delta L}{v_\beta}\left(\frac{\partial v_\beta}{\partial F}\right)_{P,T}\right]\right\}\sigma^2A^2} \tag{58}$$

Similarly the critical energy barrier is

$$\Delta G_c = (16\pi/3)\gamma^3/g = (16\pi/3)\gamma^3/(b'_o + b'_1\sigma + b'_2\sigma^2 + \ldots)^2 \tag{59}$$

$$\Delta G_c = \frac{(16\pi/3)\gamma^3}{\left\{\frac{-\Delta LA\sigma}{v_\beta} + \frac{1}{2v_\beta}\left[\left(\frac{L}{YA}\right)_\alpha - \left(\frac{L}{YA}\right)_\beta\right]\sigma^2A^2 + \left[\frac{\Delta L}{v_\beta}\left(\frac{\partial v_\beta}{\partial F}\right)_{P,T}\right]\sigma^2A^2\right\}^2} \tag{60}$$

Thus through the expansion of the free energy in a Maclaurin series one can derive expressions for the critical nucleus size and critical energy barrier for a system undergoing a first order phase transition under the influence of an applied tensile stress.

(c) Results for a second-order transition.

Likewise the expressions for r_c and ΔG_c can be found for a second-order transition by adjusting the first order expressions to be consistent with the thermodynamic criteria of second order transitions.

For a second order transition,

$$L_\alpha = L_\beta \text{ or } \Delta L = 0 \tag{61}$$

Thus the theoretical value of the critical nucleus size in a second order transition in the presence of a tensile stress is

$$r_c \simeq \frac{4\gamma Y_\alpha Y_\beta}{\sigma^2(\Delta Y)} \tag{62}$$

where $\Delta Y = Y_\beta - Y_\alpha$.

The theoretical value of the critical energy barrier is then found to be

$$\Delta G_c \simeq \frac{(64\pi/3)\gamma^3 Y_\alpha^2 Y_\beta^2}{\sigma^4(\Delta Y)^2} \tag{63}$$

4. Investigations of Polymer Solid-Liquid Interfacial Energy.

Due to the importance of the interfacial energy term in the expressions derived in the previous sections, a great deal of effort was put forth searching the literature for such data. As mentioned earlier, the interfacial energy between two "phases" in a second order transition is a quantity which customarily is believed to be zero at the normal transition point. However, as explained, the value may be non-zero at a degree of undercooling or under an applied pressure for example. Because this way of looking at this interfacial energy is somewhat novel and arises due to our particular interest in this situation, it is not surprising that mention of this quantity is not found in the literature.

However, what is surprising is that there is relatively little data available on the interfacial energy between the solid and liquid phases (γ_{SL}) in polymeric materials. As a result of this lack of data and the information collected in search of a value for the glass-rubber interfacial energy, an investigation into the problem of evaluating γ_{SL} was undertaken.

(a) Methods of determining γ_{SL} for polymers.

In this investigation, four methods were used to evaluate the liquid-solid interfacial energy. In method I, the interfacial energy was computed using the simple relationship

$$\gamma_{SL} = \gamma_S - \gamma_L \tag{64}$$

where γ_S is the solid surface tension and γ_L is the liquid surface tension. In this method γ_L was found at the melting point T_m through the use of a large amount of available data for liquid surface tension and $(\partial\gamma_L/\partial T)$. The relationship

$$\gamma_S = \left(\frac{\rho_S}{\rho_L}\right)^n \gamma_L, \tag{65}$$

where ρ_S and ρ_L are the densities of the solid and liquid phases and n is the MacLeod exponent (generally found to be about 4), was then used to compute γ_S. From the difference between γ_S and γ_L, the value of γ_{SL} is then found. The results of this method for various polymers are shown in Fig. 10a plotted against the molar heat of fusion. This type of plot is based on the work of Turnbull[16] on metals and Thomas and Stavely[17] on organics where similar plots for these materials yield straight line relationships. As a result of these linear correlations, the solid-liquid interfacial energy can easily be estimated for a class of materials with knowledge only of the molar heat of fusion, a quantity

which is much more readily available in the literature and obtainable experimentally.

As can be seen in Fig. 10, the first method does yield a somewhat linear relationship. However, this method does not account for the polarity of the polymer and thus is probably not very accurate.[18]

In method II, the polarity is considered by using a formula derived by Wu[18]:

$$\gamma_{SL} = \gamma_S + \gamma_L - \frac{4\gamma_S^d\gamma_L^d}{\gamma_S^d+\gamma_L^d} - \frac{4\gamma_S^P\gamma_L^P}{\gamma_S^P+\gamma_L^P} \tag{66}$$

where γ_S^d and γ_L^d are the dispersive components of the solid and liquid surface tension and γ_S^P and γ_L^P are the polar components of the solid and liquid surface tension. Using values given by Wu[18] for the quantities in Eq. (66) the result for γ_{SL} is shown in Fig. 10a.

The third method used to estimate γ_{SL} is that of Owens and Wendt[19]. Their equation is

$$\gamma_{SL} = \gamma_S - \gamma_c \tag{67}$$

where γ_c is the critical surface tension. Again using data given by Wu[18] for γ_c, the results are shown in Fig. 10b. It should be pointed out that the values of γ_c which were used are at 20°C and not at T_m and thus some error may have been introduced due to this fact but it is thought that the plot provides useful information.

The final method (IV) for estimating γ_{SL} is the same as that described by Turnbull[16] and Thomas and Stavely[17]. In this method, an estimate is made for the activation energy barrier and Eq. (11) is solved for the interfacial energy γ_{SL} for a certain degree of

undercooling θ. Using similar approximations to those of Turnbull[16] and Thomas and Stavely[17], the results obtained for γ_{SL} are shown in Fig. 10c.

This fourth method appears to give the best results and is by far the easiest of the four methods to obtain data and estimate γ_{SL}. Furthermore, by refining the assumptions made in the analysis, even greater accuracy may be possible.

B. Papers and Presentations

Barker, R. E., Jr., and Campbell, K. W., "Predictions of Nucleation Theory Applied to Ehrenfest Thermodynamic Transitions," J. Appl. Phys., 56 (9), 2386 (1984).

Campbell, K. W., and Barker, R. E., Jr., "Predictions of Nucleation Theory Applied to Ehrenfest Thermodynamic Transitions: II. The Effects of Pressure and Stress," to be published pending acceptance by the SPE Journal.

Abstracts

Barker, R. E., Jr., and Campbell, K. W., "Predictions of Nucleation Theory Applied to Ehrenfest Thermodynamic Transitions," Bull. Am. Phys. Soc., 29(5), 932 (1984).

Campbell, K. W., and Barker, R. E., Jr., "Considerations of the Ratio of Interfacial Energy to Specific Enthalpy of Melting for Various Classes of Materials," Va. J. Sci., 35(2), 126 (1984).

Barker, R. E., Jr., Campbell, K. W., and Huang, C. C., "Domain Growth in Polyvinylidene Fluoride Considered in Terms of Ehrenfest Transitions and Nucleation Theory," to be published, Bull. Am. Phys. Soc. (1985).

Presentations

Barker, R. E., Jr., and Campbell, K. W., "Predictions of Nucleation Theory Applied to Ehrenfest Thermodynamic Transitions," presented at the Detroit Meeting of the American Physical Society, March 26-30, 1984, Detroit, Michigan.

Campbell, K. W., and Barker, R. E., Jr., "Considerations of the Ratio of Interfacial Energy to Specific Enthalpy of Melting for Various Classes of Materials," presented at the Virginia Academy of Science Meeting, May 17, 1984, Richmond, Virginia.

Campbell, K. W., and Barker, R. E., Jr., "Predictions of Nucleation Theory Applied to Ehrenfest Thermodynamic Transitions: II. The Effects of Pressure and Stress," presented at the Symposium of Applications of Phase Diagrams in Polymer Science, National Bureau of Standards, October 15-17, 1984, Washington, D.C..

Barker, R. E., Jr., Campbell, K. W., and Huang, C. C., "Domain Growth in Polyvinylidene Fluoride Considered in Terms of Ehrenfest Transitions and Nucleation Theory," presented at the meeting of the American Physical Society, March 25-29, 1985, Baltimore, Maryland.

SECTION IV

SUMMARY AND COMMENTS

In this work we have developed a formalism for predicting the critical nucleus size and activation energy for second order Ehrenfest transitions. Correction terms are also derived for first order transitions which break from the customary approximations normally employed in classical nucleation theory. In completed work, the effects of undercoolng, hydrostatic pressure, and externally applied tensile stress have been rigorously investigated. In the case of temperature undercooling, numerical values for the critical quantities were obtained using a somewhat arbitrary range of values for γ the interfacial energy. No such attempt was made for the cases of applied pressure and stress due to the uncertainty of value for this term. Later work on this problem may have given a possible solution and method of estimating the interfacial energy between two "phases" undergoing a second order transition. This method concerns the difference in slopes of the γ vs. T curves for the different phases as described in this report. However due to the lack of γ vs. P and γ vs. σ data, such an estimate is still not possible for the other two situations described herein.

Work is now being done in which a Claussius-Clapeyron relation is used to attempt to find γ vs. P data and thereby reasonable values for the interfacial energy in the case of applied hydrostatic pressure.

Work is also continuing in which the effects of an applied electric and magnetic field are considered. It is hoped that such a situation will be more conducive to experimental investigation and thereby yield

experimental evidence for the ascertions made both in completed work and work still to be undertaken.

A number of papers and presentations have resulted from work described in this report, and our efforts are continuing in anticipation of many more fruitful developments as the research proceeds.

SECTION V

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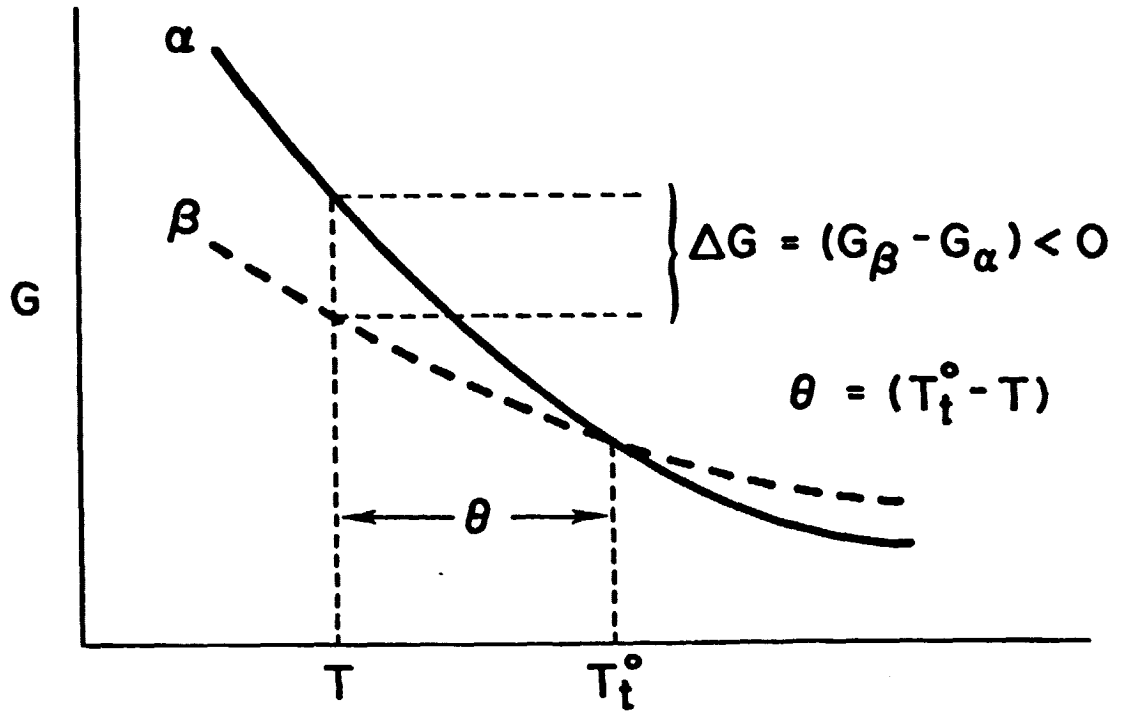
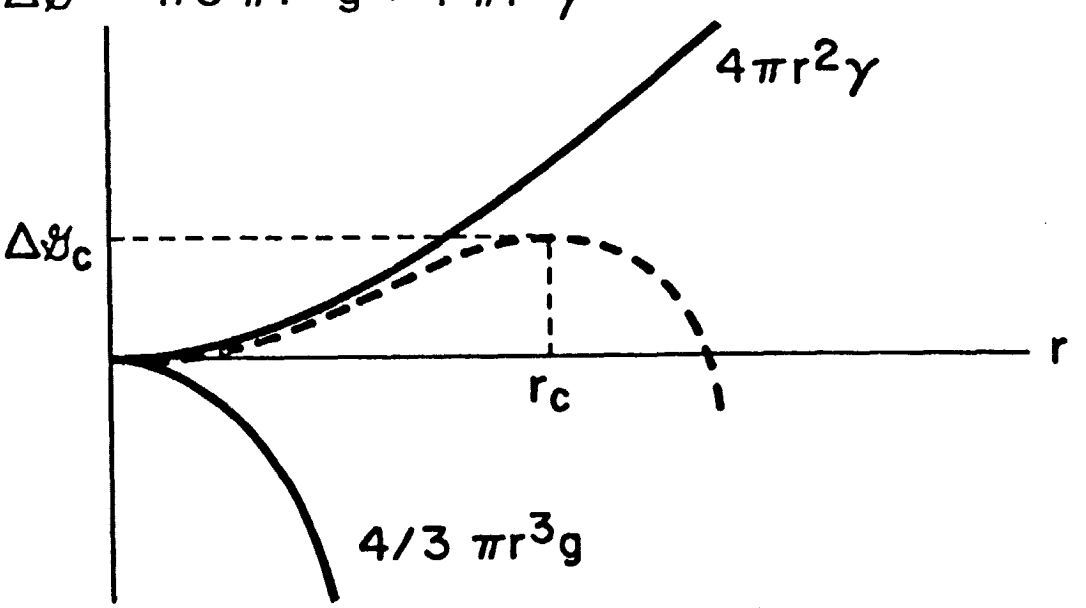


FIG. 1. For a phase transition $\alpha \rightarrow \beta$ to occur at a degree of supercooling θ, G_β must be less than G_α where G is the molar Gibbs' free energy.

$$\Delta \mathcal{G} = 4/3\,\pi r^3 g + 4\,\pi r^2 \gamma$$



$$\Delta \mathcal{G}_c \equiv \text{energy activation barrier} = 16\pi\gamma^3/3g^2$$

$$r_c \equiv \text{critical nucleus radius} = -2\gamma/g$$

FIG. 2. The two opposing energy terms which give rise to a critical radius r_c and a critical energy barrier ΔG_c for nucleation.

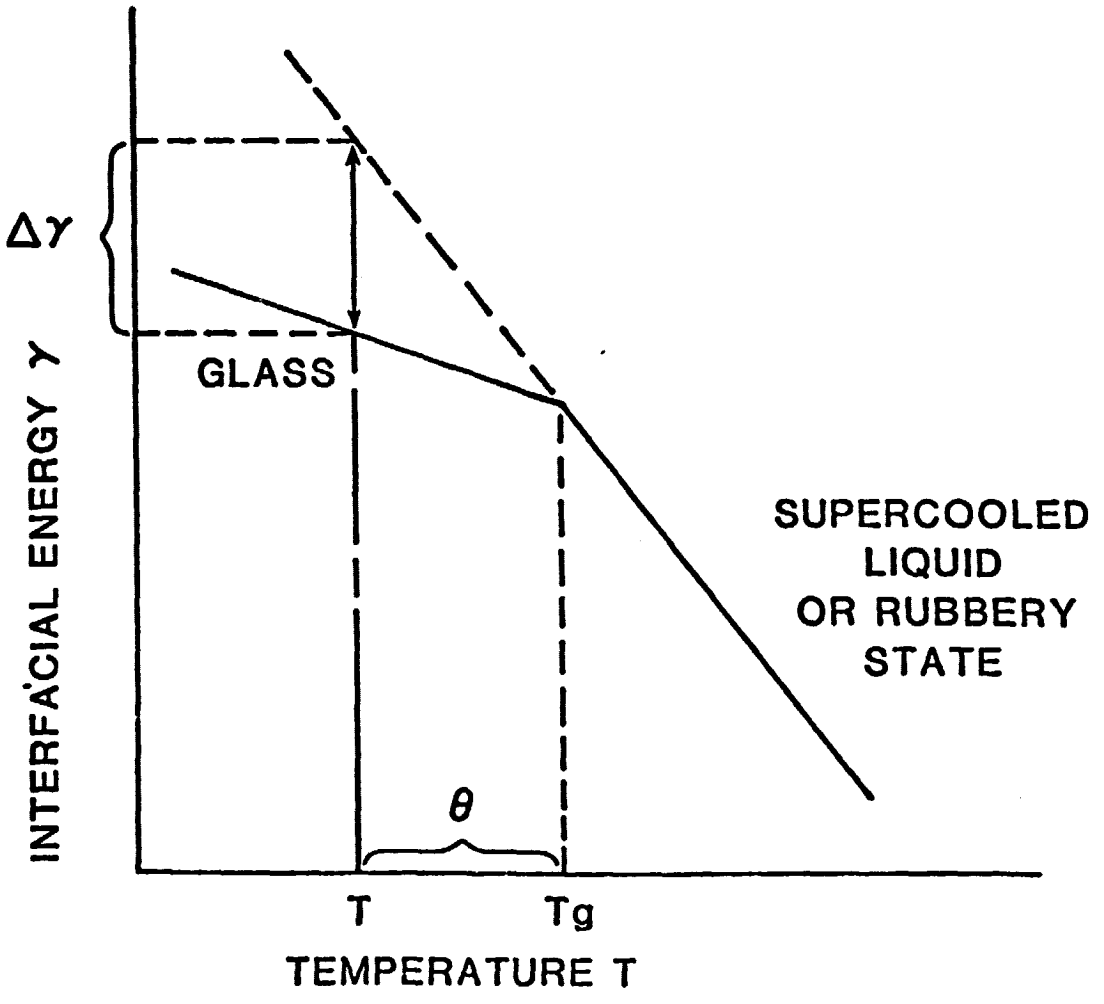


FIG. 3. Schematic representation of a method to estimate the effective interfacial energy for an undercooled system if $\gamma_g = \gamma_r$.

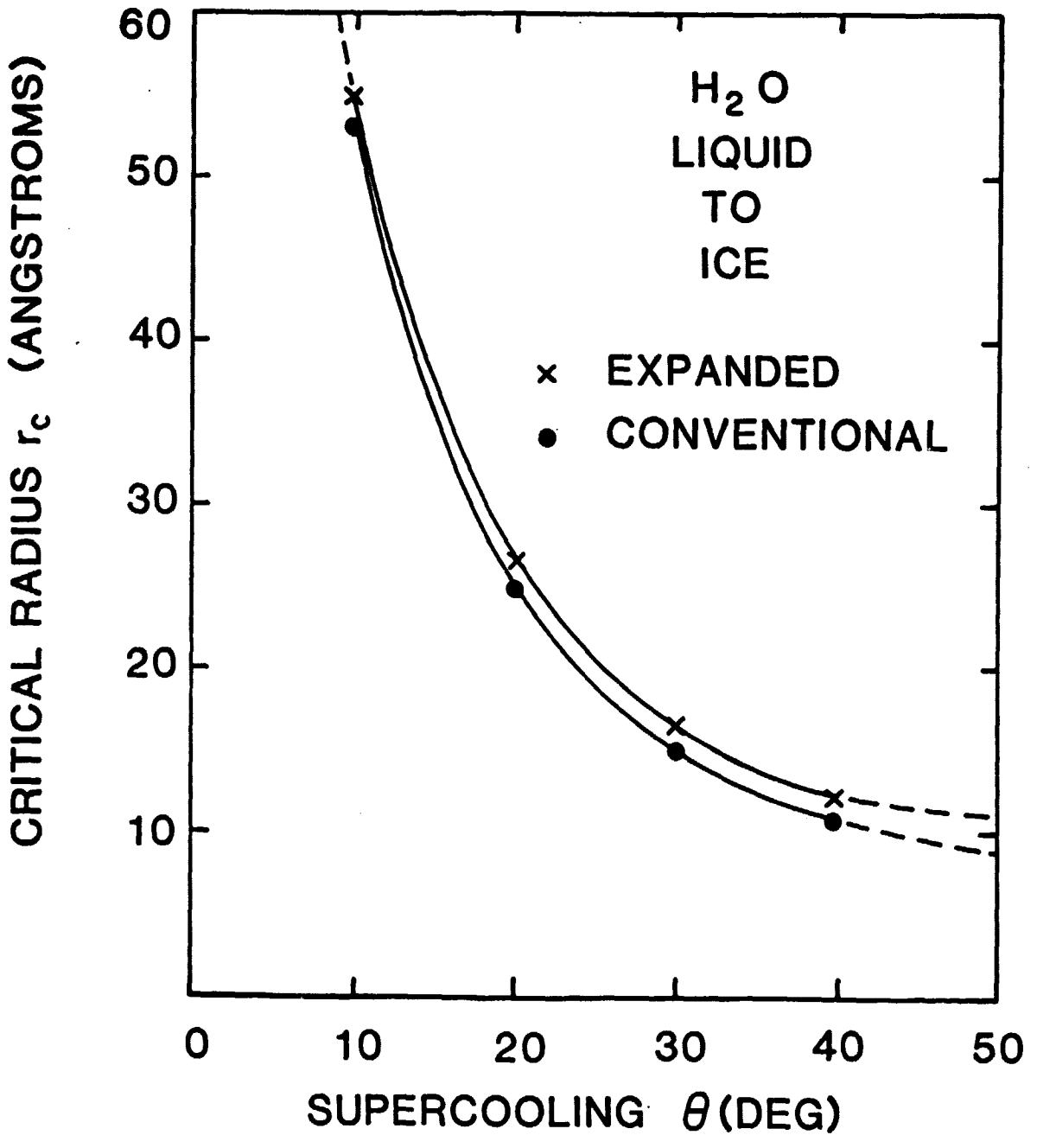


FIG. 4. The dependence of critical nucleus size on the degree of supercooling for the transition of liquid water to ice for both the conventional and expanded approaches.

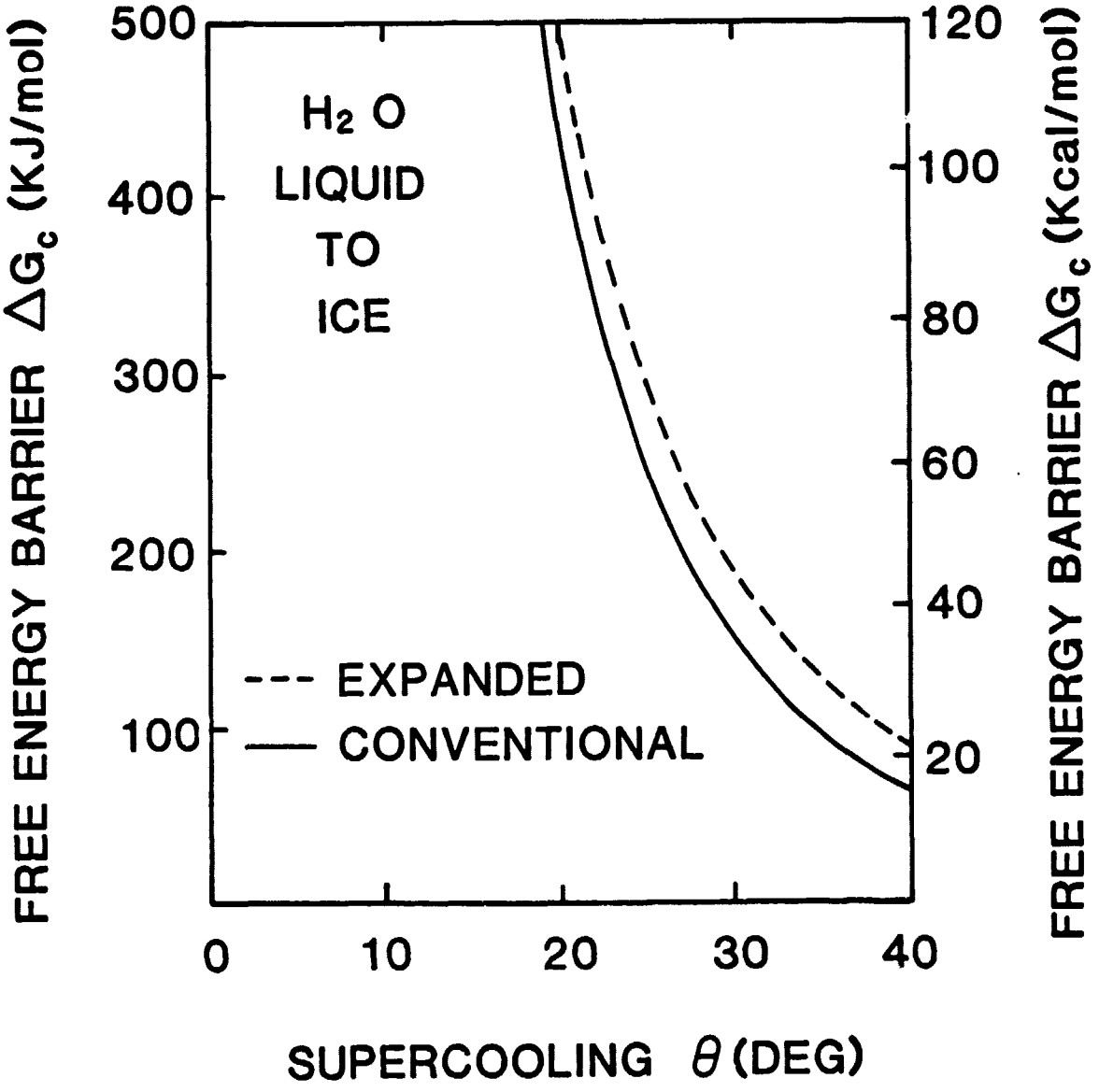


FIG. 5. The dependence of the free energy barrier on the degree of supercooling for the transition of liquid water to ice for both the conventional and expanded approaches.

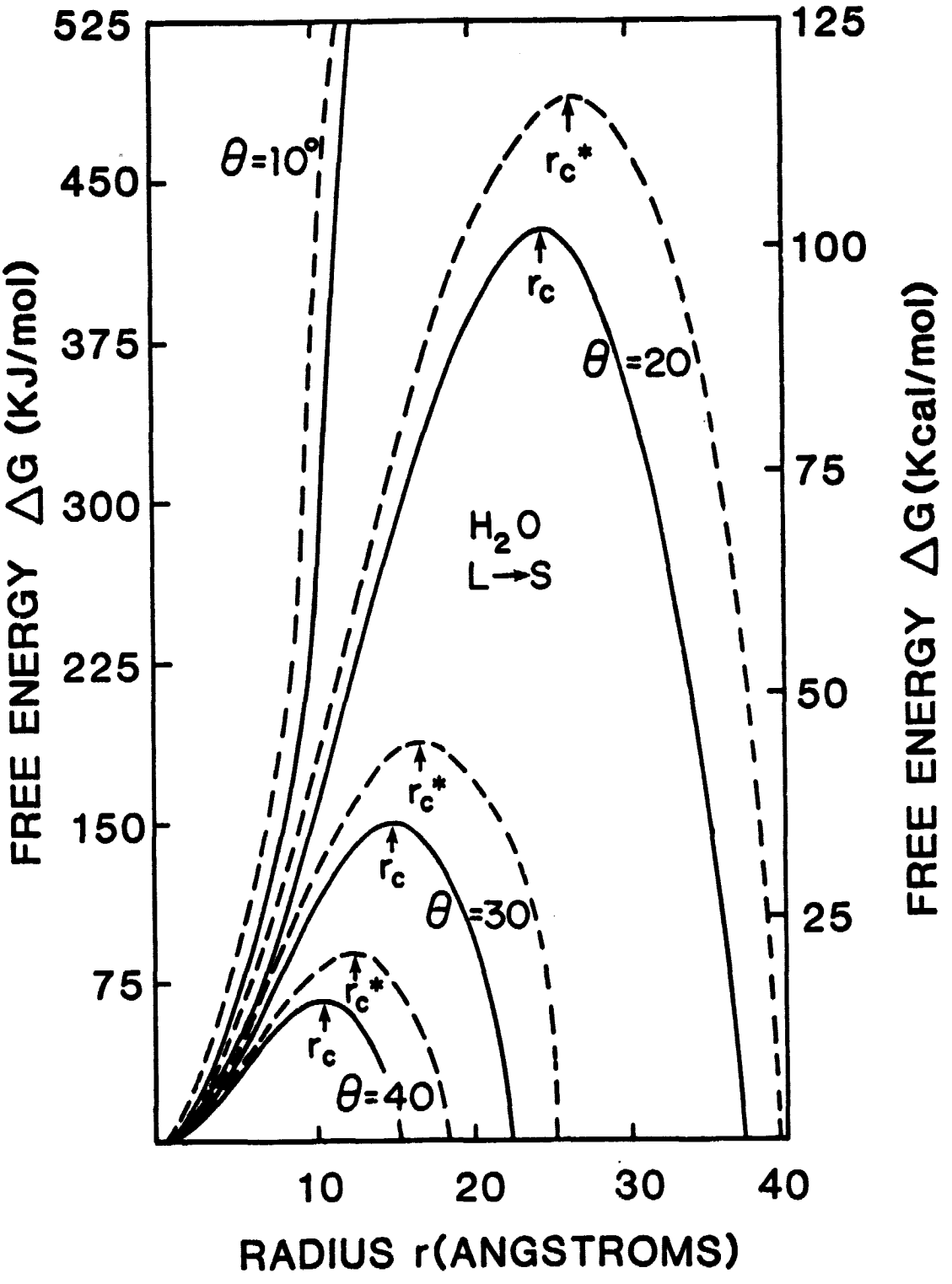


FIG. 6. The free energy as a function of cluster size for various degrees of supercooling for the transition of liquid water to ice for both the conventional (solid curve) and expanded (dashed curve) approaches.

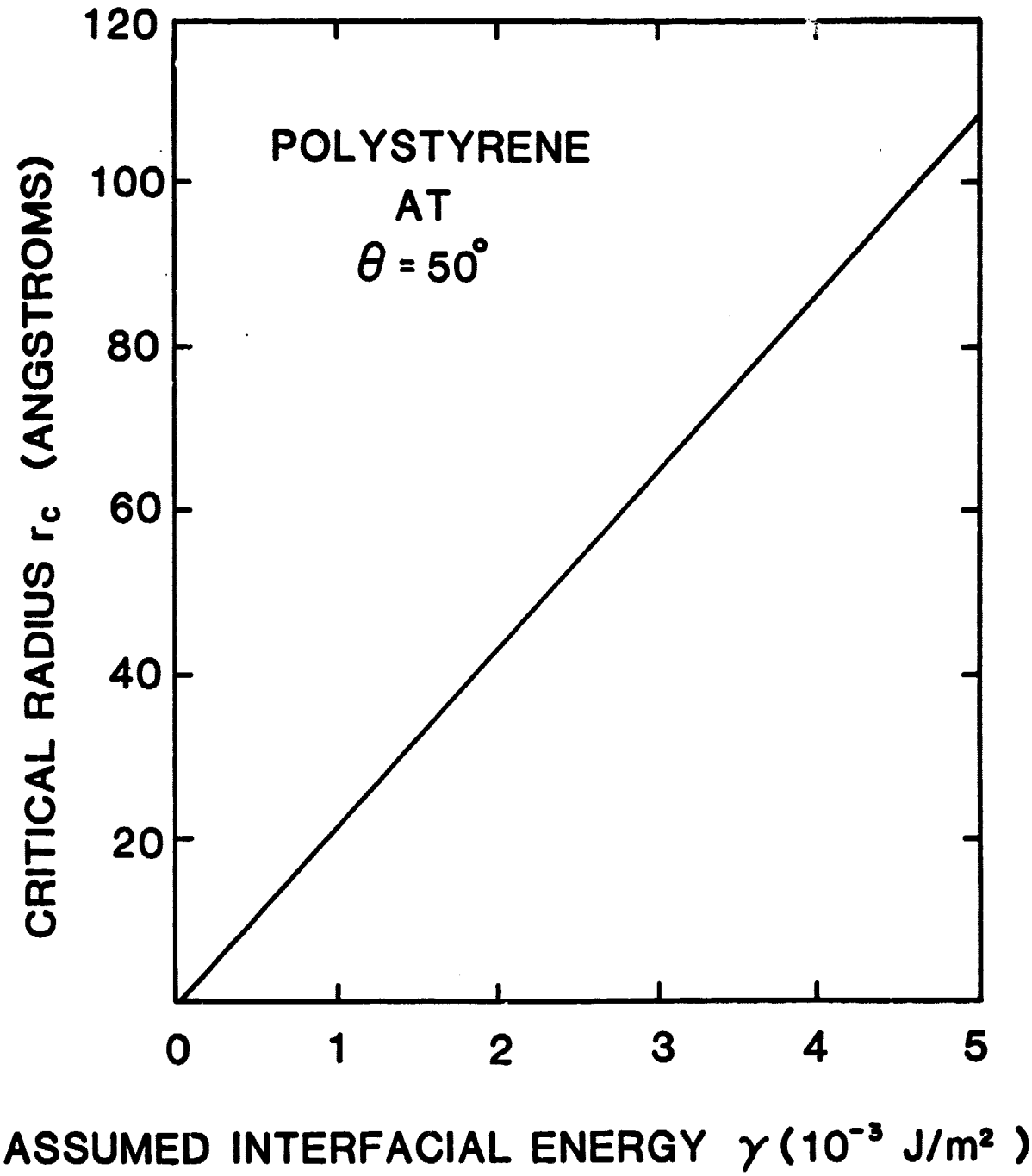


FIG. 7. The critical nucleus size as a function of assumed interfacial energy for the glass transition of polystyrene at a supercooling of 50 deg.

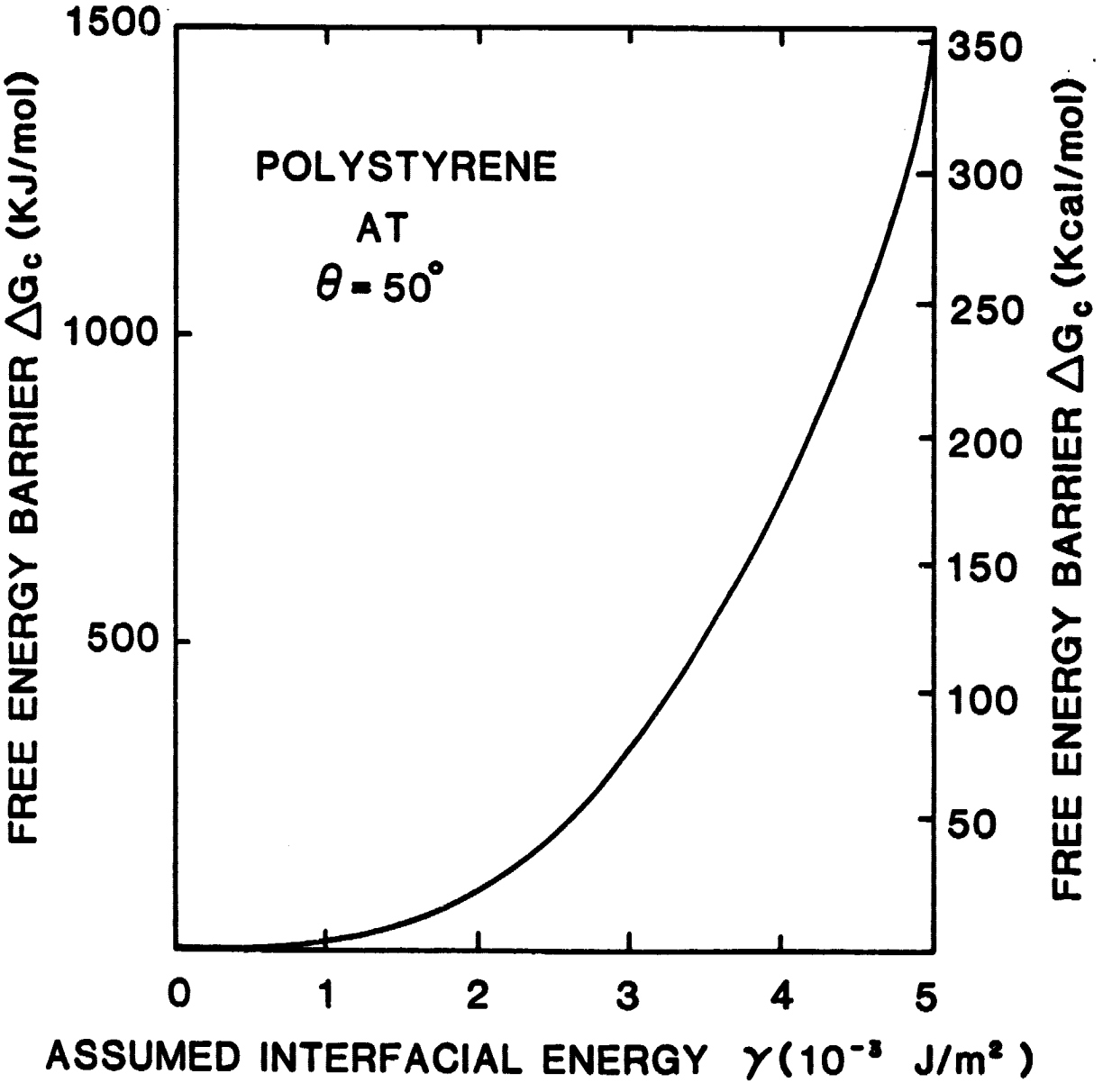


FIG. 8. The free energy barrier as a function of assumed interfacial energy for the glass transition of polystyrene at a supercooling of 50 deg.

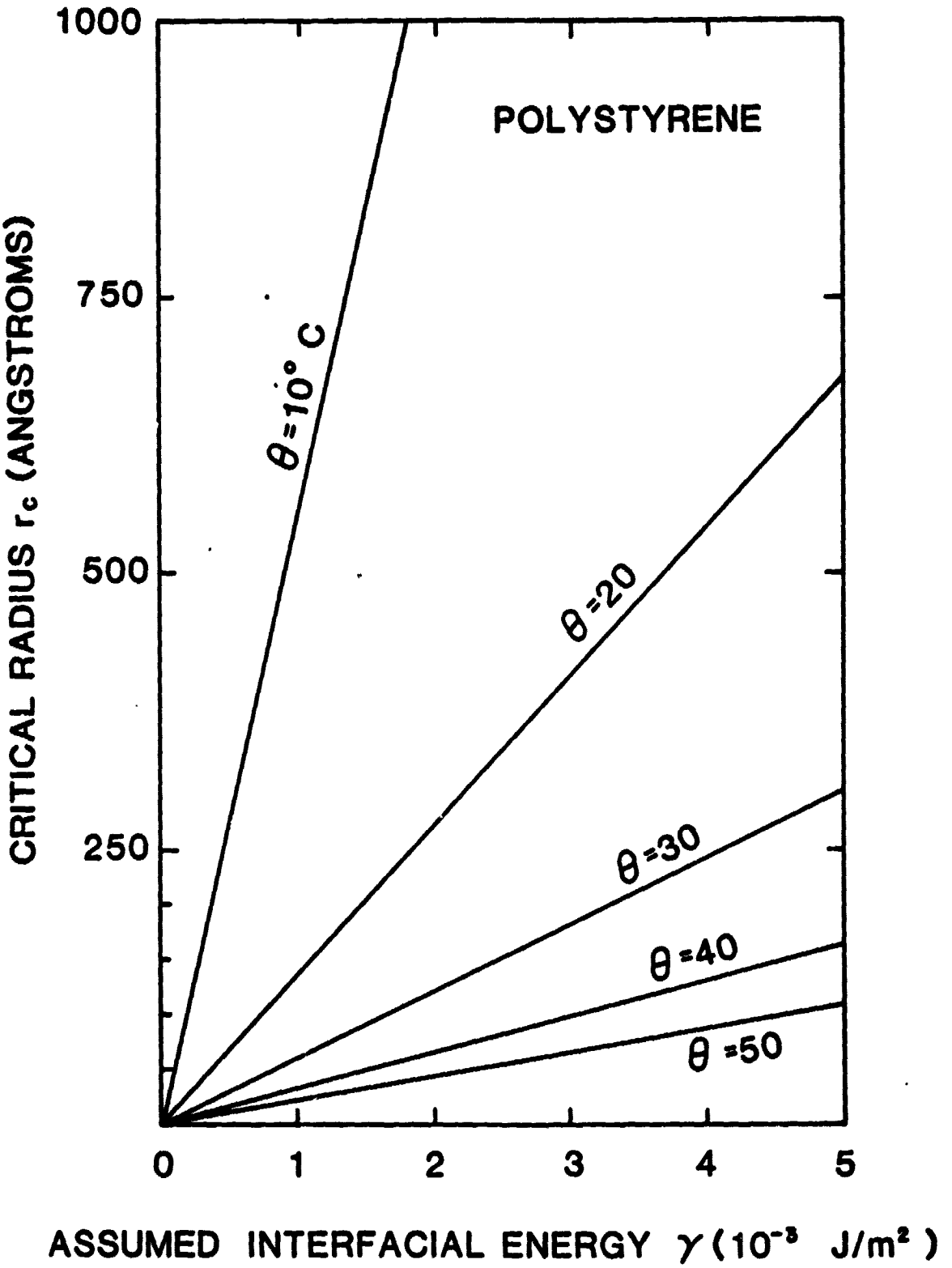


FIG. 9. The critical nucleus size as a function of assumed interfacial energy of various degrees of supercooling for the glass transition of polystyrene.

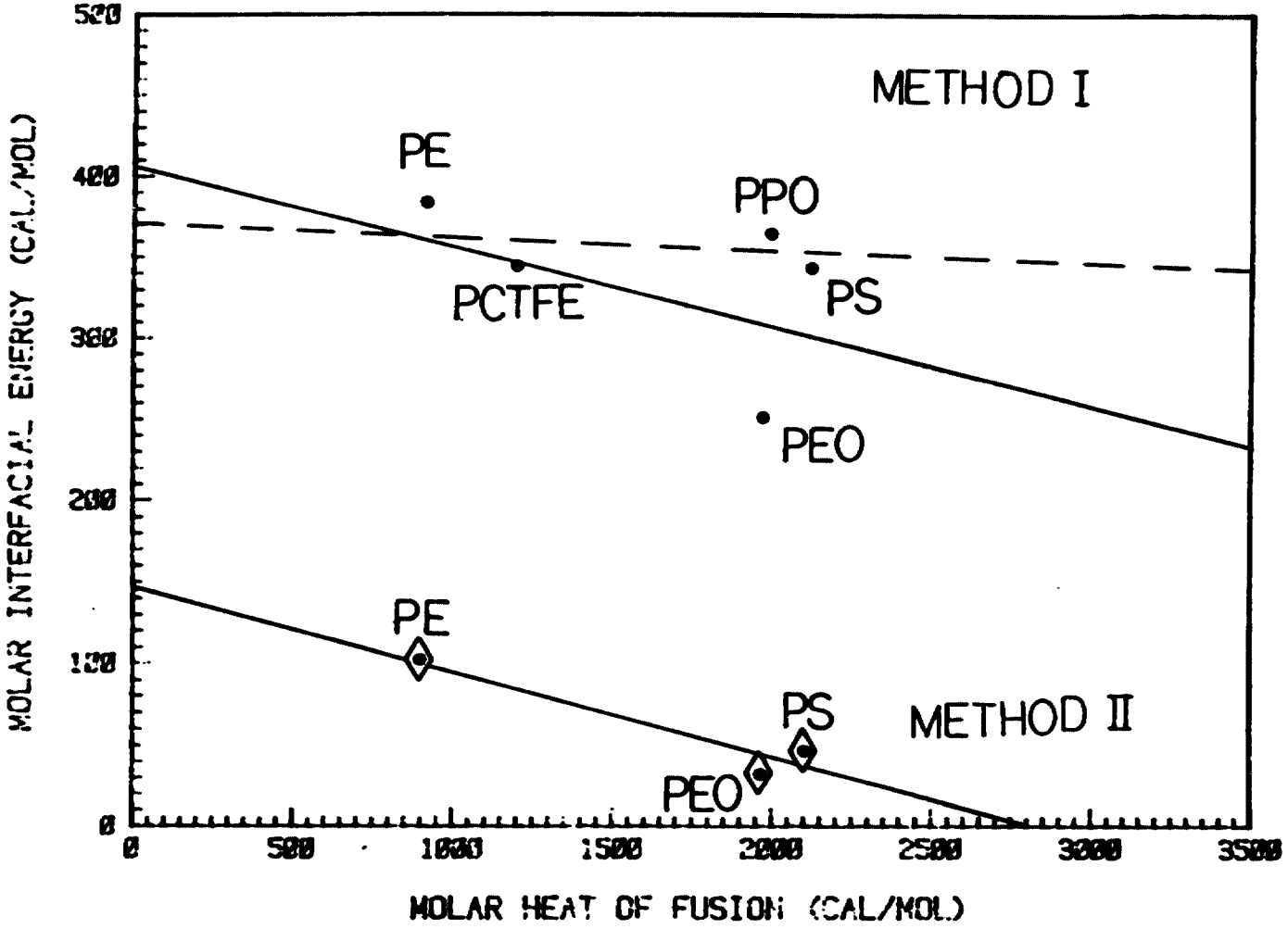


FIG. 10a. The relationship between the molar interfacial energy and the molar heat of fusion for various polymers calculated using (i) Method I where $\gamma_{SL} = \gamma_S - \gamma_L$ and (ii) Method II where

$$\gamma_{SL} = \gamma_S + \gamma_L - \frac{4\gamma_S^d\gamma_L^d}{\gamma_S^d+\gamma_L^d} - \frac{4\gamma_S^P\gamma_L^P}{\gamma_S^P+\gamma_L^P}$$

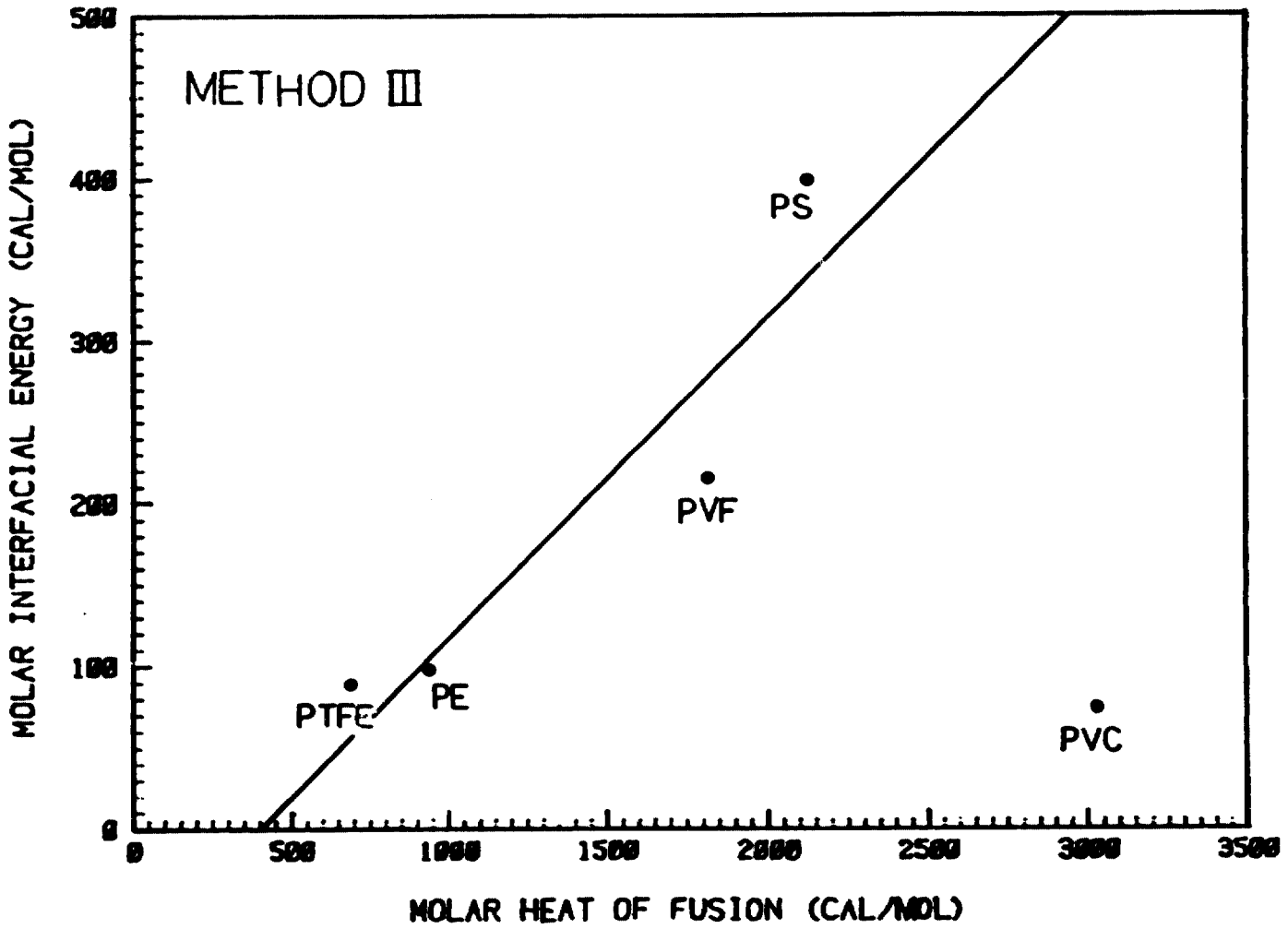


FIG. 10b. (iii) Method III where $\gamma_{SC} = \gamma_S - \gamma_C$.

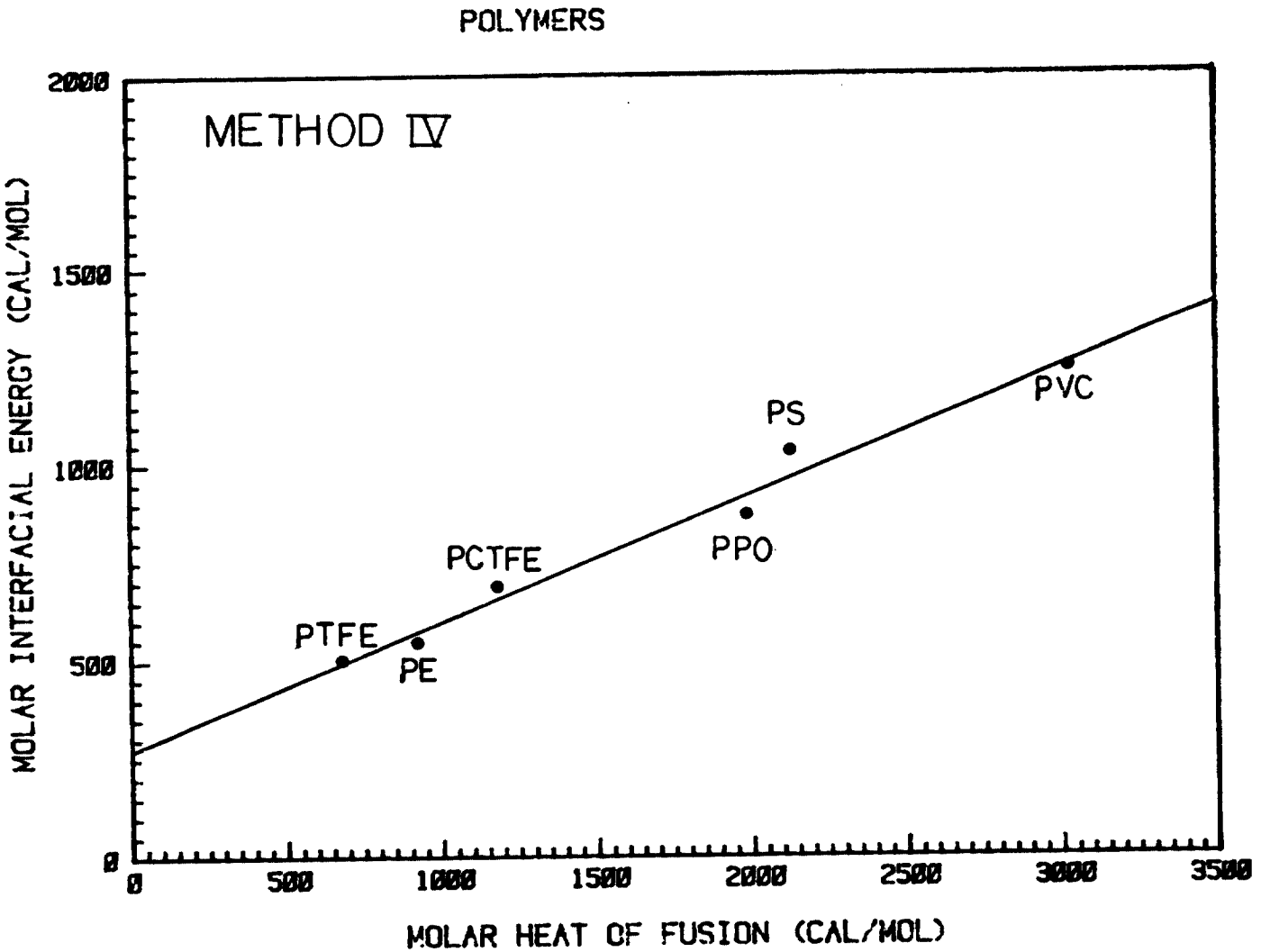


FIG. 10c. (iv) Method IV where the method of Turnbull[16] is used to estimate γ_{SC} from nucleation theory.

SECTION VI

APPENDIX

Abstracts and Manuscripts Recently Submitted for Publication

Predictions of nucleation theory applied to Ehrenfest thermodynamic transitions : II. The effects of pressure and stress.

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(Received

Abstract

This paper is a sequel to an earlier one, BC-I (J. Appl. Phys. 56, 2386 (1984)), on the applicability of classical nucleation theory to second-order transitions in the Ehrenfest sense. In each case the approach was to obtain the critical size r_c and energy barrier ΔG_c for the growth of a nucleus of β-phase in an α-phase matrix by a Maclaurin series expansion of the free-energy-density $g=(G_\beta-G_\alpha)/v_\beta$ as a function of θ (in BC-I) and of ΔP and $\Delta\sigma$ in this paper where $\theta=(T-T_t)$ is the degree of undercooling and ΔP and $\Delta\sigma$ are analogous terms for the hydrostatic pressure shift and tensile stress shift away from the equilibrium transition. The expansion coefficients were determined by the use of thermodynamic relationships. For second-order transitions, $r_c=4\gamma v_\beta T_t/\Delta C_p\theta^2$, $r_c=4\gamma/\Delta\beta(\Delta p)^2$, and $r_c=4\gamma Y_\alpha Y_\beta/\Delta Y(\Delta\sigma)^2$, respectively for the three cases. The terms ΔC_p, $\Delta\beta$, and ΔY denote the differences in heat capacity, compressibility, and Young's modulus, e.g., $\Delta Y=Y_\beta-Y_\alpha$. The interfacial energy $\gamma_{\alpha\beta}$ is denoted by γ. The activation energy barriers for the cases developed in this paper were $\Delta G_c=(16\pi/3)\gamma^3/(\Delta\beta)^2(\Delta p)^4$ and $\Delta G_c=(64\pi/3)\gamma^3 Y_\alpha^2 Y_\beta^2/(\Delta Y)^2(\Delta\sigma)^4$. More complicated expressions are given in the paper for the r_c and ΔG_c for first-order transitions. In the long run these expressions may prove more useful than the ones for second-order because of the modifications expressions for the kinetics of transformations.

where V_β is the volume of the β nucleus, v_β is the molar volume and $A_{\alpha\beta}$ is the interfacial area of β. If the growing nucleus has more than one type of interface, then the term $A_{\alpha\beta}\,\gamma_{\alpha\beta}$ would imply a summation over the relevant areas. In the present paper, an extra term, corresponding to the elastic strain energy when v_α is not equal to v_β in solid phases, will be neglected.

Thus, according to nucleation theory, local density fluctuations will lead to the formation of a small nucleus of β phase within an α-phase matrix if the temperature is less than the normal transition temperature T_t for $\alpha \rightleftharpoons \beta$ where β is the stable phase when $T < T_t$ (Fig. 1). The total interfacial energy $A_{\alpha\beta}\,\gamma_{\alpha\beta}$ will oppose the enlargement of the nucleus, and a bulk-free energy gV_β will encourage growth (Fig. 2). The term

$$g = (G_\beta - G_\alpha)/v_\beta \tag{3}$$

represents the free energy change per unit volume of *transformed* material. Equation (2) now becomes

$$\Delta \mathcal{G} = gV_\beta + \gamma A_\beta. \tag{4}$$

C. The customary approximations

In the standard treatments, $\Delta G = \Delta H - T\Delta S$ is approximated, at a degree of undercooling

$$\theta = T_t - T \tag{5}$$

by $\Delta H = \Delta H_t$ and $\Delta S = \Delta H_t/T_t$ which may be seen to give

$$\Delta G = \Delta S_t \theta, \quad \text{with } S_t = \Delta H_t/T_t \tag{6}$$

or

$$g = s_t\theta, \quad \text{with } s_t = \Delta S_t/v_\beta. \tag{7}$$

The standard treatments next proceed by taking $\partial(\Delta G)/\partial r = 0$, where r is the radius of the spherical nucleus for which

$$V_\beta = (4/3)\pi r^3 \text{ and } A_\beta = 4\pi r^2. \tag{8}$$

This gives the size of the critical nucleus r_c to be

$$r_c = -2\gamma/g. \tag{9}$$

For the stable $\alpha \rightarrow \beta$ transition, g will be negative ($g = 0$ for the equilibrium transition). Substitution of Eq. (9) back into Eq. (4) gives the usual type of expression for the "activation barrier" that must be overcome before the continued growth of the β nucleus can take place.

$$\Delta \mathcal{G}_c = (16\pi/3)\gamma^3/g^2 = 16.76\,\gamma^3/g^2. \tag{10}$$

This barrier, and the critical size r_c, are of course both dependent on the degree of undercooling, through Eq. (7), therefore

$$r_c = -2\gamma/s_t\theta = \frac{-2\gamma(T_t/\theta)}{h_t} \tag{11}$$

and

$$\Delta \mathcal{G}_c = (16\pi/3)\gamma^3/s_t^2\theta^2 = \frac{(16\pi/3)\gamma^3(T_t/\theta)^2}{(h_t)^2}, \tag{12}$$

where $h_t = \Delta H_t/v_\beta$ is the latent heat per unit volume for the transformation at standard pressure.

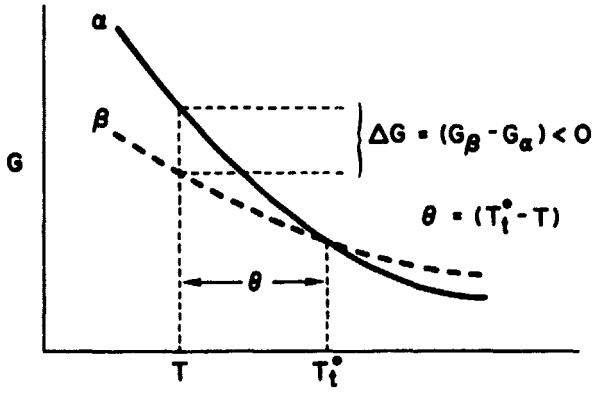
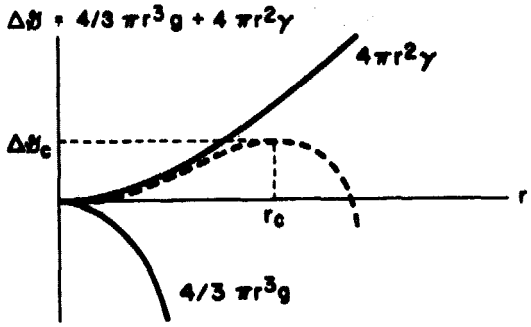


FIG. 1. For a phase transition $\alpha \rightarrow \beta$ to occur at a degree of supercooling θ, G_β must be less than G_α where G is the molar Gibbs' free energy.



$\Delta \mathcal{G}_c \equiv$ energy activation barrier $= 16\pi\gamma^3/3g^2$

$r_c \equiv$ critical nucleus radius $= -2\gamma/g$

FIG. 2. The two opposing energy terms which give rise to a critical radius r_c and a critical energy barrier $\Delta \mathcal{G}_c$ for nucleation.

NEW THEORETICAL APPROACH

A description will now be given for a mathematical formulation of nucleation theory in which the customary approximations discussed earlier are avoided. The result is a number of expressions which are unobtainable using the conventional methods.

A. Proposal of a more rigorous approach

The twelve equations above summarize an elementary view of homogeneous nucleation theory for the special case of spherical particles. The need for a more rigorous formalism in which the customary approximations are not applied is evident. In this new theory, such a formalism is developed through the assumption that $\Delta \mathcal{G}$ and therefore g can be expanded in a Maclaurin's series in θ, the degree of undercooling. This series is then reduced and manipulated through the use of Maxwell's relations and other thermodynamic operations. As a result of this rigorous treatment, the following features are developed: (1) nonlinear correction terms result for first-order thermodynamic transitions, (2) the critical nucleus size and barrier height for second-order transitions (in the Ehrenfest sense), and (3) the possibility of a formal extension of nucleation theory to even higher-order transitions. Since the new theory brings in the higher-order effects as analytic thermodynamic terms (rather than merely

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mathematical or empirical approximations) it is a more flexible theory for predicting other effects, such as the influence of changes in pressure, stress, electric field, etc. The new theory, for the same reason, should also be more amenable to the incorporation of ideas from statistical mechanics; and to compositional and kinetic extensions such as Couchman's[8] T_g theory and the time-temperature-transformation concepts of Enns and Gillham.[9]

B. Central features of the new approach

As outlined in the previous section it is possible to construct a useful, and apparently overlooked, formalism by what in its barest form is the expedient of expanding the effective free energy of the transformed nucleus in a Maclaurin series in θ (the degree of undercooling), *and then* ultilizing thermodynamical relations to evaluate the expansion coefficients. For example, if we take

$$g = g(\theta) = g(0) + g'(0)\theta + (1/2)g''(0)\theta^2 + \ldots$$
$$= a_0 + a_1\theta + a_2\theta^2 + \ldots \tag{13}$$

then $g'(0)$, which means $(\partial g/\partial\theta)_p$ at $\theta = 0$, can be found as follows,

$$\left(\frac{\partial g}{\partial \theta}\right)_p = \left(\frac{\partial g}{\partial T}\right)_p \left(\frac{\partial T}{\partial \theta}\right)_p = -\left(\frac{\partial g}{\partial T}\right)_p, \tag{14}$$

but

$$G_\beta - G_\alpha = H_\beta - H_\alpha - T(S_\beta - S_\alpha), \tag{15}$$

so that

$$g \equiv (G_\beta - G_\alpha)/v_\beta = h - Ts, \tag{16}$$

where

$$h \equiv (H_\beta - H_\alpha)/v_\beta \text{ and } s \equiv (S_\beta - S_\alpha)/v_\beta. \tag{17}$$

Carrying through the operations required,

$$\left(\frac{\partial g}{\partial T}\right)_p = \frac{1}{v_\beta}\left[\left(\frac{\partial G_\beta}{\partial T}\right)_p - \left(\frac{\partial G_\alpha}{\partial T}\right)_p\right] - \frac{1}{v_\beta^2}(G_\beta - G_\alpha)\left(\frac{\partial v_\beta}{\partial T}\right)_p \tag{18}$$

$$= -\frac{1}{v_\beta}(S_\beta - S_\alpha) - g\alpha_\beta, \tag{19}$$

where use has been made of the thermodynamic relations $S = -(\partial G/\partial T)_p$ and thermal expansivity $= \alpha = (\partial v/\partial T)_p/v$.

C. Calculations of the coefficients

Further reduction of Eq. (18) gives

$$\left(\frac{\partial g}{\partial T}\right)_p = -\frac{h}{T} - g\left(\frac{\partial \alpha_\beta}{\partial T}\right)_p, \tag{20}$$

and thus, using Eq. (13) at $T = T_t$ or $\theta = 0$, we obtain

$$a_1 = g'(0) \equiv \left(\frac{\partial g}{\partial \theta}\right)_p\Big|_{\theta=0} = +\frac{h_t}{T_t}, \tag{21}$$

because $g(0)$ is zero (when $T = T_t$). In a similar fashion, it can be shown that

$$g''(\theta) = -\frac{1}{v_\beta}\left(\frac{\partial S_\beta}{\partial T} - \frac{\partial S_\alpha}{\partial T}\right)_p + \frac{\alpha_\beta}{v_\beta}(S_\beta - S_\alpha) - \alpha_\beta\left(\frac{\partial g}{\partial T}\right)_p - g\left(\frac{\partial \alpha_\beta}{\partial T}\right)_p. \tag{22}$$

After some reduction, Eq. (22) evaluated at $\theta = 0$ gives

$$g''(0) = -\frac{(C_p)_\beta - (C_p)_\alpha}{v_\beta T_t} + \frac{2\alpha_\beta h_t}{T_t}. \tag{23}$$

An examination of Eqs. (12)–(23) reveals that

$$a_0 = 0, \quad a_1 = h/T_t,$$
$$a_2 = -(\Delta C_p/2v_\beta h_t) + (\alpha_\beta h_t/T_t), \ldots \tag{24}$$

RESULTS

The results obtained through the series expansion will now be discussed. These results will be interpreted for both first- and second-order Ehrenfest transitions. These mathematical results will then be used to give semiquantitative results for both classes of transitions in representative systems.

A. First-order transitions

A revisitation of Eq. (9) with the incorporation of the expansion derived in the previous sections gives a critical nucleus

$$r_c = -2\gamma/g = -2\gamma/(a_1\theta + a_2\theta^2 + \ldots), \tag{25}$$

$$r_c = -\frac{2\gamma(T_t/\theta)}{h_t}\frac{1}{1 - [(\Delta C_p/2v_\beta h_t) - \alpha_\beta]\theta + \ldots}, \tag{26}$$

where h_t is a negative number for an exothermic transition.

Similarly, incorporation of Eq. (10) with the expanded results gives an activation energy barrier

$$\Delta \mathcal{G}_c = (16\pi/3)\gamma^3/g^2 = (16\pi/3)\gamma^3/(a_1\theta + a_2\theta^2 + \ldots)^2, \tag{27}$$

$$\Delta \mathcal{G}_c = \frac{(16\pi/3)\gamma^3(T_t/\theta)^2}{(h_t)^2} \times \frac{1}{1 - [(\Delta C_p/2v_\beta h_t) - \alpha_\beta]^2\theta^2 + \ldots}. \tag{28}$$

These equations reduce to the conventional expressions given in Eqs. (11) and (12) when the higher-order correction terms are neglected. Thus as a result of the expansion of the free energy in a Taylor series, we have explicit, convenient, and (in principle) experimentally accessible correction factors for first order homogeneous nucleation theory.

B. Second-order transitions

In a second-order Ehrenfest transition, since the latent heat is zero, the conventional expressions given in Eqs. (11) and (12) are physically meaningless because in both cases the denominator is zero. However, using the results derived in the preceeding section for r_c and $\Delta \mathcal{G}_c$, meaningful results for the critical nucleus size and critical activation energy for second-order transitions can be determined. Thus evaluating Eq. (26) for the case where $h_t = 0$ gives a critical nucleus

$$r_c = \frac{4\gamma v_\beta T_t}{(\Delta C_p)\theta^2}. \tag{29}$$

Similarly, evaluating Eq. (28) for the case where $h_t = 0$ gives an activation energy barrier

$$\Delta \mathcal{G}_c = \frac{(64\pi/3)\gamma^3 v_\beta^2 T_t^2}{(\Delta C_p)^2 \theta^4}. \tag{30}$$

There is evidence that the interfacial energy $\gamma = \gamma_{\alpha\beta}$ between phases separated by a second-order transition may have a zero value at the equilibrium second-order transition temperature.[10] However on the basis of our continuing investigation we suspect that at a degree of undercooling $\theta = T - T_t$, which is the point of concern in the present argument, γ will not vanish because the curves for the total surface energies $\gamma(\alpha)$ and $\gamma(\beta)$ have different slopes $\partial\gamma(\alpha)/\partial T$ and $\partial\gamma(\beta)/\partial T$. In the case of the glass transition in polymers where $T_t = T_g$, α corresponds to the rubbery (liquid) state and β to the glassy state. The underlying physical phenomenon is the existence of molecular fluctuation which give rise to the formation of a small embryo.

Hence a mathematical formulation for applying classical nucleation theory to second-order Ehrenfest transitions is found through the expansion of the Gibbs' free energy in a Maclaurin series.

C. Numerical results

A semiquantitative graphical representation of the results is given in Figs. 3–8 using typical data for the first-order liquid to solid transition of water and the quasi-second-order glass transition of polysytrene. In Fig. 3 and Fig. 4 the critical parameters for a first-order transition are plotted against the degree of supercooling using both the conventional and expanded approaches. These plots serve to give an order of magnitude estimation as to the size of the "correction factor" discussed earlier. Figure 5 shows a relationship similar

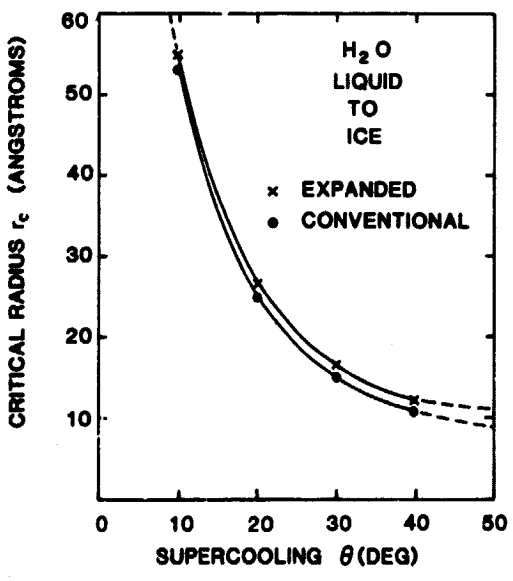


FIG. 3. The dependence of critical nucleus size on the degree of supercooling for the transition of liquid water to ice for both the conventional and expanded approaches.

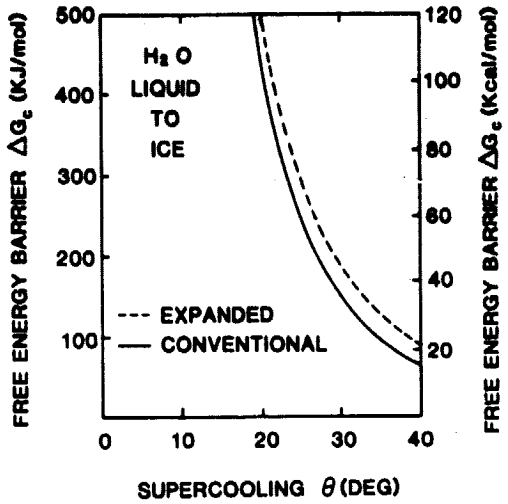


FIG. 4. The dependence of the free energy barrier on the degree of supercooling for the transition of liquid water to ice for both the conventional and expandcd approaches.

to the qualitative representation of Fig. 2 in which the free energy is plotted against the cluster size for various degrees of supercooling. The peak of each curve gives the values for r_c and G_c. The values of the data were collected from various sources in the literature and are listed in Refs. 11 and 12.

Figures 6 and 7 graphically show the size of the critical parameters as a function of assumed interfacial energy between the glassy and rubbery states of polystyrene at a fifty degree supercooling. The use of an assumed interfacial energy is a consequence of the lack of data of this type in the literature. The values chosen, although somewhat arbitrary, are believed to be of the proper magnitude for such systems. Figure 8 shows the variation of the critical nucleus size with

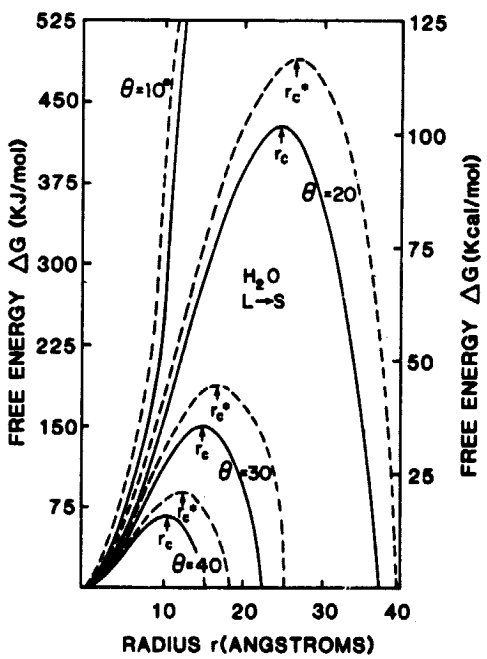


FIG. 5. The free energy as a function of cluster size for various degrees of supercooling for the transition of liquid water to ice for both the conventional (solid curve) and expanded (dashed curve) approaches.

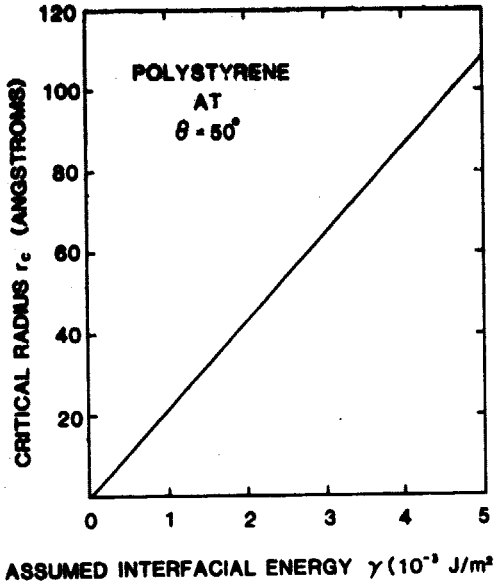


FIG. 6. The critical nucleus size as a function of assumed interfacial energy for the glass transition of polystyrene at a supercooling of 50 deg.

the assumed interfacial energy for various degrees of supercooling. The source of the data plotted for polystyrene is given in Refs. 13 and 14.

As indicated above, appropriate experimental data for the interfacial energy $\gamma_{\alpha\beta} = \gamma$ are not presently available. Therefore we have chosen γ as an independent variable for graphical representation in Figs. 6, 7, and 8. Current research efforts are directed toward the determination of appropriate values of γ. These plots serve to provide guides for the design of relevant experiments to measure this interfacial energy.

CONCLUSION

In this paper we have developed a formalism for predicting the critical nucleus size and the activation energy barrier for second-order Ehrenfest transitions. Correction terms are also derived for first-order transitions which break from the customary approximations normally employed in classical nucleation theory. A semiquantitative analysis of this new approach was then presented to give a physical sense to the theoretical relations. Thus as a result of expanding the Gibbs' free energy in a Maclaurin series, a mathematical model is developed for applying classical nucleation theory to second-order Ehrenfest transitions.

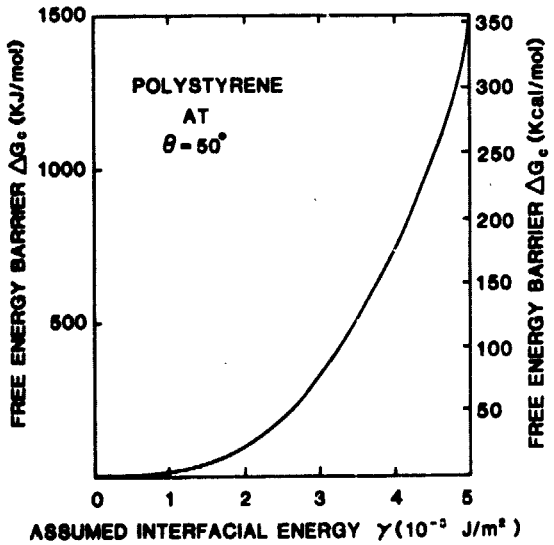


FIG. 7. The free energy barrier as a function of assumed interfacial energy for the glass transition of polystyrene at a supercooling of 50 deg.

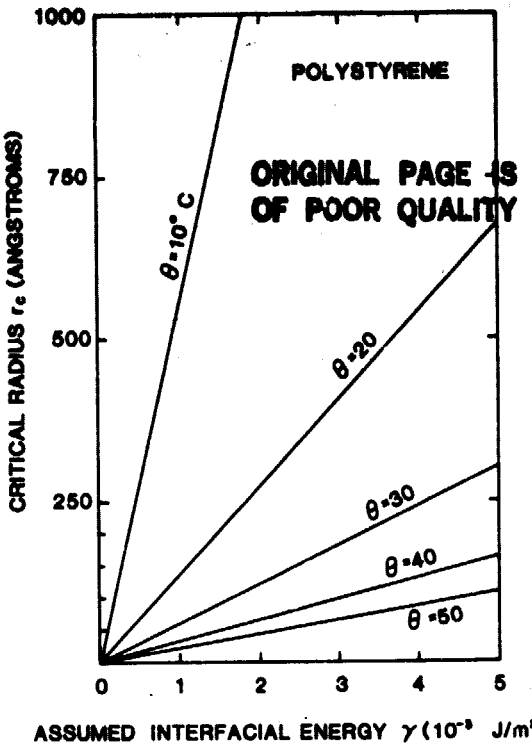


FIG. 8. The critical nucleus size as a function of assumed interfacial energy of various degrees of supercooling for the glass transition of polystyrene.

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Predictions of nucleation theory applied to Ehrenfest thermodynamic transitions : II. The effects of pressure and stress.

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Abstract

This paper is a sequel to an earlier one, BC-I (J. Appl. Phys. 56, 2386 (1984)), on the applicability of classical nucleation theory to second-order transitions in the Ehrenfest sense. In each case the approach was to obtain the critical size r_c and energy barrier ΔG_c for the growth of a nucleus of β-phase in an α-phase matrix by a Maclaurin series expansion of the free-energy-density $g=(G_\beta-G_\alpha)/v_\beta$ as a function of θ (in BC-I) and of ΔP and $\Delta\sigma$ in this paper where $\theta=(T-T_t)$ is the degree of undercooling and ΔP and $\Delta\sigma$ are analogous terms for the hydrostatic pressure shift and tensile stress shift away from the equilibrium transition. The expansion coefficients were determined by the use of thermodynamic relationships. For second-order transitions, $r_c=4\gamma v_\beta T_t/\Delta C_p\theta^2$, $r_c=4\gamma/\Delta\beta(\Delta p)^2$, and $r_c=4\gamma Y_\alpha Y_\beta/\Delta Y(\Delta\sigma)^2$, respectively for the three cases. The terms ΔC_p, $\Delta\beta$, and ΔY denote the differences in heat capacity, compressibility, and Young's modulus, e.g., $\Delta Y=Y_\beta-Y_\alpha$. The interfacial energy $\gamma_{\alpha\beta}$ is denoted by γ. The activation energy barriers for the cases developed in this paper were $\Delta G_c=(16\pi/3)\gamma^3/(\Delta\beta)^2(\Delta p)^4$ and $\Delta G_c=(64\pi/3)\gamma^3 Y_\alpha^2 Y_\beta^2/(\Delta Y)^2(\Delta\sigma)^4$. More complicated expressions are given in the paper for the r_c and ΔG_c for first-order transitions. In the long run these expressions may prove more useful than the ones for second-order because of the modifications expressions for the kinetics of transformations.

Introduction

In a previous paper (BC-I)[1] on this general subject, a formalism was developed for the application of classical nucleation theory to first- and second-order thermodynamic transitions ($\alpha \rightarrow \beta$) in the Ehrenfest sense. This was accomplished through the expansion of the Gibbs' free energy in a Maclaurin series in the degree of supercooling θ. By using this approach, significantly improved expressions were obtained for the size r_c and the energy barrier ΔG_c of the critical nucleus for first-order transitions. Moreover, physically meaningful expressions also were obtained for r_c and ΔG_c for a system undergoing a second-order phase transition with the assumption that, in such a transition (e.g., order-disorder, normal-superconducting, and (approximately) the glass transition in polymers), the new phase does not occur spontaneously throughout the matrix but rather begins locally as nuclei which grow until the transformation $\alpha \rightarrow \beta$ is complete. For this approach, the existence of an effective interfacial energy $\gamma = \gamma_{\alpha\beta}$ between the two "phases" (or states of aggregation) is essential. However in the usual theories of second-order transitions γ is believed to be zero at the equilibrium transition temperature T_t.[2] For the purposes of the present analysis we postulate that the type of transformation of interest ($\alpha \rightarrow \beta$) occurs under non-equilibrium (supercooled) conditions with a small but nonvanishing γ. Furthermore, by the application of pressure, tensile stress, or electric, or magnetic fields of sufficient magnitude, the free energy curves G_α and G_β (for certain first-order transitions) which cross at more that one point may possibly be shifted to produce a common tangent, thus simulating a second-order transition. These situations

(supercooling and shifted free energy) thus lead to the possibility of nucleation and growth processes for quasi-second-order transitions.

A formalism similar to that utilized in BC-I, wherein the excess free energy density $g=(G_\beta-G_\alpha)/v_\beta$ was expressed in terms of the degree of undercooling, will now be developed in terms of applied pressure p and tensile stress σ. The results for the application of electric and magnetic fields will be given in a subsequent presentation. The present derivation, in terms of p and σ, will be preceded by a brief outline of certain relevant features of classical nucleation theory (CNT), with references to appropriate literature sources for more detailed descriptions of the ideas and facts, especially about nucleation phenomena involved with polymeric materials.

The paper concludes with a discussion of the results that are obtained and the implications of these results when applied to real systems.

Review of Classical Nucleation Theory

Before discussing the detailed derivation of the expressions of interest in this work, a short review of CNT as it applies to this case is in order. For a more complete description of classical nucleation theory and phase transitions especially as applied to polymeric materials see references 1, 3-9.

A. The thermodynamic basis of nucleation theory

As is widely known, when a pure system of molecules which exists as a stable phase α at a given set of intensive variables (T_1,p_1, etc.), is subjected to new intensive conditions (T_2,p_2, etc.), where α is no longer the only stable phase but where one or more new phases are

stable, then it is possible that the expected transformation $\alpha \rightarrow \beta$ will occur only slowly, if at all, within a finite observation period. According to the precepts of nucleation theory, the reason for this inhibition of the expected transformation is that molecular fluctuations and diffusive motion must occur which create a small particle of β within the α milieu (but see Ref. 9) and that there is an interface between the α and β regions in which the molecules have an excess free energy $\gamma=\gamma_{\alpha\beta}$ per unit area. Thus the true Gibbs free energy change corresponding to the transformation of a small amount of α into a small nucleus of β is not merely the so-called bulk thermodynamic value ΔG (energy per mole); it is instead

$$\Delta G=V_{\beta}(\Delta G/\upsilon_{\beta})+A_{\alpha\beta}\gamma_{\alpha\beta} \qquad (1)$$

where V_{β} is the volume of the β nucleus, υ_{β} is the molar volume and $A_{\alpha\beta}$ is the interfacial area of β. If the growing nucleus has more than one type of interface, then the term $A_{\alpha\beta}\gamma_{\alpha\beta}$ would imply a summation over the relevant areas. In the present paper, an extra term, corresponding to the elastic strain energy when υ_{α} is not equal to υ_{β} in solid phases, will be neglected.

Thus, according to nucleation theory, a small nucleus of β phase will form within an α-matrix if the free energy curve of the β phase is lower than the free energy curve of the α-phase. This can be accomplished in several ways, for example by supercooling below the normal transition temperature T_t (Fig. 1a), or by the application of an external pressure (Fig. 1b), or the application of a tensile stress (Fig. 1c).

Under such conditions the total interfacial energy $A_{\alpha\beta}\gamma_{\alpha\beta}$ will oppose the enlargement of the nucleus and a bulk free energy gV_β will encourage growth (Fig. 2). The term

$$g \equiv (G_\beta - G_\alpha)/v_\beta \tag{2}$$

represents the free energy change per unit volume of the transformed material. Equation (1) now becomes

$$\Delta G = gV_\beta + \gamma A_\beta . \tag{3}$$

B. Results for a spherical nucleus

In much but not all of the literature the nuclei of β-phase are assumed to be spherical for simplicity. This assumption will be used in this paper since we are presently more concerned with the qualitative features of the phenomenon, and its very existence, than with detailed quantitative refinements, related to nucleus shape, which we will address in subsequent presentations.

In order to determine the critical parameters r_c and ΔG_c shown in Fig. 2., the free energy is differentiated with respect to the radius r and the result is set equal to zero.

$$\delta(\Delta G)/\delta r = 0 \text{ at } r = r_c . \tag{4}$$

The resulting expression for r is termed the critical radius, i.e., the radius that an embryo must exceed in order for its growth to be favorable. For a spherical nucleus where

$$V_\beta = (4/3)\pi r^3 \text{ and } A_\beta = 4\pi r^2 \tag{5}$$

the size of the critical nucleus is found to be

$$r_c = -2\gamma/g \tag{6}$$

This value, substituted into Eq. (4), gives the critical activation energy barrier,

$$\Delta G_c = (16\pi/3)\gamma^3/g^2, \tag{7}$$

that is the energy barrier which inhibits the continued growth of the β phase.

New Extension of the Theory

The preceeding basic precepts of nucleation theory can be applied to both first- and second-order thermodynamic transitions under the influence of applied hydrostatic pressure and more complicated stress fields.

A. Basic concepts of the new approach

In this new approach a formalism for predicting the effects of applied pressure and applied stress on r_c and ΔG_c for a phase transition of any order is developed through the assumption that ΔG and therefore g can be expanded in a Maclaurin series. The coefficients in the series are then obtained through the use of Maxwell's relations and other thermodynamic operations. Relatively simple expressions result, involving experimentally accessible parameters, which describe the effect of applied pressure and stress on the critical quantities ΔG_c and r_c. More importantly these expressions yield physically meaningful (non-zero) results for ΔG_c and r_c when the derived results are reduced

in accord with the theory of second order transitions. These two main aspects of the theory will now be described in detail, first for the case of applied pressure and then for the case of applied stress.

B. Predicted effects of hydrostatic pressure

As outlined earlier, the main point of the theory is the expansion of the free energy in a Maclaurin series.

This expansion in terms of $\Delta P=P-P_o$, where P_o is the initial pressure of the system, may be expressed as follows

$$g = g(\Delta P) = g(0) + g'(0)\Delta P + \frac{1}{2} g''(0)(\Delta P)^2 + \ldots \quad (8)$$

$$= b_0 + b_1 \Delta P + b_2 (\Delta P)^2 + \ldots \quad (9)$$

where, for example, $b_1=g'(0)=(\partial g/\partial P)_T$ evaluated at $\Delta P=0$. It should be noted that g is also a function of temperature and thus g evaluated at $\Delta P=0$ is not necessarily zero unless the function is also evaluated at the normal temperature for the transition at the initial pressure of the system. Alternately stated, the function is also evaluated at a degree of supercooling θ equaling zero as in BC-I.[1] Thus for example a system which is initially at atmospheric pressure (P_o=latm.), g(0) equals zero when the function is evaluated both at $P=P_o$ or $\Delta P=0$ and at the normal transition temperature $T=T_t^o$ or $\theta=0$. Since this is the case in the present discussion, $b_o=g(0)$ in Eq.(9) will be zero.

From the definition $g=\Delta G/v_\beta$ and relations such as $v_\alpha=(\partial G_\alpha/\partial P)_T$, and $\beta_\alpha=-(\partial \ln v_\alpha/\partial P)_T$ for the volume and compressibility of the α-phase, it follows that

$$g'(0) \equiv \left(\frac{\partial g}{\partial \Delta P}\right)_T = \left(\frac{\partial g}{\partial P}\right)_T = \frac{1}{v_\beta}\left[\left(\frac{\partial G_\beta}{\partial P}\right)_T - \left(\frac{\partial G_\alpha}{\partial P}\right)_T\right] - \left[\left(\frac{G_\beta - G_\alpha}{v_\beta^2}\right)\left(\frac{\partial v_\beta}{\partial P}\right)_T\right]\Bigg|_{\Delta P=0} \qquad (10)$$

Thus at $\Delta P=0$ and $\theta=0$ we have

$$g'(0) = b_1 = \frac{v_\beta - v_\alpha}{v_\beta} = \frac{\Delta v}{v_\beta} \qquad (11)$$

where $\Delta u = u_\beta - u_\alpha$. Note that $G_\beta - G_\alpha$ in Eq (10) is zero for the reasons discussed previously.

In a similar way,

$$g''(0) = \frac{1}{v_\beta}\left[\left(\frac{\partial v_\beta}{\partial P}\right)_T - \left(\frac{\partial v_\alpha}{\partial P}\right)_T\right] - \frac{1}{v_\beta^2}\left[(v_\beta - v_\alpha)\left(\frac{\partial v_\beta}{\partial P}\right)_T\right] + \left[g\left(\frac{\partial \beta_\beta}{\partial P}\right)_T + \left(\frac{\partial g}{\partial P}\right)_T \beta_\beta\right]\Bigg|_{\Delta P=0} \qquad (12)$$

After reduction and evaluation at $\Delta P=0$ and $\theta=0$

$$\tfrac{1}{2} g''(0) = b_2 = \tfrac{1}{2}\left[\frac{v_\alpha}{v_\beta}(\beta_\alpha - \beta_\beta) + \frac{(v_\beta - v_\alpha)\beta_\beta}{v_\beta}\right] \qquad (13)$$

Summarizing the results of the expansion

$$g(0) = b_0 = \left.\frac{\Delta G}{v_\beta}\right|_{\Delta P=0} = 0 \tag{14}$$

$$g'(0) = b_1 = \frac{v_\beta - v_\alpha}{v_\beta} = \frac{\Delta v}{v_\beta} \tag{15}$$

$$b_2 = \frac{1}{2}\left(-\frac{v_\alpha}{v_\beta}\Delta\beta + \frac{\beta_\beta}{v_\beta}\Delta v\right) \tag{16}$$

C. Results for a first-order transition

Use can now be made of Eqs.(6) and (7) by incorporating the results of the free energy expansion to obtain expressions for the critical nucleus size and critical energy barrier for a first-order transition occurring isothermally under the influence of an applied pressure. The critical nucleus size is found from Eq.(6) to be

$$r_c = 2\gamma/g = -2\gamma/(b_0 + b_1\Delta P + b_2(\Delta P)^2 + \ldots) \qquad (17)$$

$$r_c \approx \frac{-2\gamma}{\frac{\Delta v}{v_\beta}\Delta P - \left[\frac{1}{2}\left(\frac{v_\alpha}{v_\beta}\Delta\beta - \frac{\beta_\beta}{v_\beta}\Delta v\right)\right](\Delta P)^2 + \ldots} \qquad (18)$$

Similarly the critical energy barrier is found to be

$$\Delta \mathcal{G}_c = \frac{(16\pi/3)\gamma^3}{\left[\frac{\Delta v}{v_\beta}\Delta P - \frac{1}{2}\left(\frac{v_\alpha}{v_\beta}\Delta\beta - \frac{\beta_\beta}{v_\beta}\Delta v\right)(\Delta P)^2\right]^2} \qquad (19)$$

Thus relatively simple expressions have been found for r_c and ΔG_c for phase transitions induced by the application of pressure.

D. Results for second-order transitions

As in the previous section, expressions for r_c and ΔG_c can be found for second-order transitions which occur in the presence of an applied pressure. For a second-order transition

$$V_\alpha = V_\beta \qquad \text{OR} \quad \Delta V = 0 \tag{20}$$

so that the value of g reduces to

$$-\frac{1}{2}\Delta\beta(\Delta P)^2 \tag{21}$$

Therefore the theoretical value of r_c in a second-order transition, induced by applied pressure, is found to be

$$r_c \approx \frac{4\gamma}{\Delta\beta(\Delta P)^2} \tag{22}$$

Similarly, the theoretical value for the critical energy barrier is

$$\Delta \mathcal{H}_c \approx \frac{(64\pi/3)\gamma^3}{(\Delta\beta)^2(\Delta P)^4} \tag{23}$$

E. Mathematical development in terms of stress

The same type of derivation which was carried out for the case of applied pressure will now be developed for the application of a tensile stress. Although very similar in some respects to the previous case, there are some important differences which require a rather detailed presentation, rather than merely treating the stress as a negative pressure. Starting in the same way as for Eq.(8) we have

$$g = g(\sigma) = g(0) + g'(0)\sigma + \frac{1}{2} g''(0)\sigma^2 + \ldots \qquad (24)$$

$$= b'_0 + b'_1\sigma + b'_2\sigma^2 + \ldots \qquad (25)$$

where $\sigma = F/A_o$ is the nominal stress and $g'(o)$ denotes $(\partial g/\partial\sigma)_{P,T}$ at $\sigma=0$. This derivative can be expressed as follows

$$\left(\frac{\partial g}{\partial \sigma}\right)_{P,T} = \left(\frac{\partial g}{\partial F}\right)_{P,T} \left(\frac{\partial F}{\partial \sigma}\right)_{P,T} = A_o \left(\frac{\partial g}{\partial F}\right)_{P,T} \qquad (26)$$

where A_o is the initial cross-sectional area.

Carrying through the required operations

$$g'(0) \equiv \left(\frac{\partial g}{\partial \sigma}\right)_{P,T} = A\left(\frac{\partial g}{\partial F}\right)_{P,T} = A\left\{\frac{1}{v_\beta}\left[\left(\frac{\partial G_\beta}{\partial F}\right)_{P,T} - \left(\frac{\partial G_\alpha}{\partial F}\right)_{P,T}\right] - \left[\left(\frac{G_\beta - G_\alpha}{v_\beta^2}\right)\left(\frac{\partial v_\beta}{\partial F}\right)_{P,T}\right]\right\}\Bigg|_{\sigma=0} \tag{27}$$

Use will now be made of the thermodynamic relation $(\partial G/\partial F)_{P,T} = -L$.

Thus at $\sigma=0$ or $F=0$ we have

$$g'(0) = b_1' = A\left[\frac{-(L_\beta - L_\alpha)}{v_\beta}\right] = \frac{-\Delta L}{v_\beta} A \tag{28}$$

where $\Delta L = L_\beta - L_\alpha$ and $g(0)$ is zero when $\sigma=0$ or $F=0$.

In a similar fashion, it can be shown that

$$g''(0) = \left(\frac{\partial^2 g}{\partial F^2}\right)A^2\Big|_{\sigma=0} = A^2\left\{\frac{1}{v_\beta}\left[\left(\frac{\partial L_\alpha}{\partial F}\right)_{P,T} - \left(\frac{\partial L_\beta}{\partial F}\right)_{P,T}\right] - \left[\frac{(L_\alpha - L_\beta)}{v_\beta^2}\left(\frac{\partial v_\beta}{\partial F}\right)_{P,T}\right]\right.$$

$$\left. - \left[\frac{v_\beta\left(\frac{\partial g}{\partial F}\right)_{P,T} - g\left(\frac{\partial v_\beta}{\partial F}\right)_{P,T}}{v_\beta^2}\right]\left(\frac{\partial v_\beta}{\partial F}\right)_{P,T} + \left[\left(\frac{g}{v_\beta}\right)\left(\frac{\partial^2 v_\beta}{\partial F^2}\right)_{P,T}\right]\right\}_{\sigma=0} \tag{29}$$

After reduction, Eq (29) evaluated at $\sigma=0$ gives

$$\frac{1}{2}g''(0) = b'_2 = \left\{ \frac{1}{2v_\beta}\left[\left(\frac{L}{YA}\right)_\alpha - \left(\frac{L}{YA}\right)_\beta\right] + \left[\left(\frac{\Delta L}{v_\beta^2}\right)\left(\frac{\partial v_\beta}{\partial F}\right)_{P,T}\right]\right\} A^2 \qquad (30)$$

where use has been made of the relation $(\partial L/\partial F)=L/YA_o$ where Y is the Young's modulus.

Collecting the resulting coefficients,

$$g(0) = b'_0 = \frac{\Delta G}{v_\beta}\bigg|_{\sigma=0} = 0 \qquad (31)$$

$$g'(0) = b'_1 = A\left[\frac{-(L_\beta - L_\alpha)}{v_\beta}\right] = \frac{-\Delta L}{v_\beta} A \qquad (32)$$

$$\frac{1}{2}g''(0) = b'_2 = \left\{ \frac{1}{2v_\beta}\left[\left(\frac{L}{YA}\right)_\alpha - \left(\frac{L}{YA}\right)_\beta\right] + \left[\left(\frac{\Delta L}{v_\beta^2}\right)\left(\frac{\partial v_\beta}{\partial F}\right)_{P,T}\right]\right\} A^2 \qquad (33)$$

F. Results for a first order transition

Following the procedure outlined in section C, for the case of applied pressure, one can find the expressions for r_c and ΔG_c for the case of applied stress.

$$r_c = -2\gamma/g = -2\gamma/(b'_0 + b'_1\sigma + b'_2\sigma^2 + \ldots) \qquad (34)$$

$$r_c \approx \frac{-2\gamma}{-\left(\frac{\Delta L A \sigma}{V_\beta}\right) + \left\{\frac{1}{2V_\beta}\left[\left(\frac{L}{YA}\right)_\alpha - \left(\frac{L}{YA}\right)_\beta\right] + \left[\frac{\Delta L}{V_\beta}\left(\frac{\partial V_\beta}{\partial F}\right)_{P,T}\right]\right\}\sigma^2 A^2} \qquad (35)$$

Similarly the critical energy barrier is

$$\Delta\mathcal{H}_c = (16\pi/3)\,\gamma^3/g = (16\pi/3)\,\gamma^3/(b'_0 + b'_1\sigma + b'_2\sigma^2 + \ldots)^2 \qquad (36)$$

$$\Delta\mathcal{H}_c \approx \frac{(16\pi/3)\gamma^3}{\left\{\frac{-\Delta L A \sigma}{V_\beta} + \frac{1}{2V_\beta}\left[\left(\frac{L}{YA}\right)_\alpha - \left(\frac{L}{YA}\right)_\beta\right]\sigma^2 A^2 + \left[\frac{\Delta L}{V_\beta}\left(\frac{\partial V_\beta}{\partial F}\right)_{P,T}\right]\sigma^2 A^2\right\}^2} \qquad (37)$$

Thus through the expansion of the free energy in a Maclaurin series one can derive expressions for the critical nucleus size and critical energy barrier for a system undergoing a first-order phase transition under the influence of an applied tensile stress.

G. Results for a second-order transition

Likewise the expressions for r_c and ΔG_c can be found for a second-order transition by adjusting the first-order expressions to be consistent with the thermodynamic criteria of second-order transitions.

For a second-order transition,

$$L_\alpha = L_\beta \text{ OR } \Delta L = 0 \qquad (38)$$

Thus the theoretical value of the critical nucleus size in a second-order transition in the presence of a tensile stress is

$$r_c \approx \frac{4\gamma Y_\alpha Y_\beta}{\sigma^2(\Delta Y)} \qquad (39)$$

where $\Delta Y = Y_\beta - Y_\alpha$.

The theoretical value of the critical energy barrier is then found to be

$$\Delta \mathcal{H}_c \approx \frac{(64\pi/3)\gamma^3 Y_\alpha^2 Y_\beta^2}{\sigma^4(\Delta Y)^2} \qquad (40)$$

Discussion and Conclusions

The mathematical basis for the application of classical nucleation theory to second-order thermodynamic transitions has been demonstrated. However, a number of points should be addressed in connection with the derived results. The expressions for r_c and ΔG_c in both the case of applied pressure and stress contain an interfacial energy term γ. In the case of an equilibrium second-order transition this term vanishes.[2] However, our contention is that under non-equilibrium conditions, such as described here and in Ref. 1, there is a small interfacial energy

difference associated with the region between the α and β-phases, for example between aggregations of different degrees of order. The question then arises whether such a transition should still be considered to be second-order in nature. It is our belief that the order classification of the transition should remain the same due to the fact that the transition itself is unchanged. However the kinetics are likely to be considerably altered.

Our analysis has shown that thermodynamic concepts do not appear to preclude the nucleation and growth of a new phase in a second-order transition in Ehrenfest's classification. In fact reasonable expressions for the size and energy barrier in terms of measurable quantities result. However it may be that the likelihood is small for actually finding a set of conditions for which the predicted nucleation and growth can be observed. Even if this turns out to be the case, the results that we have derived suggest quite significant effects on the kinetics of first-order transitions.

It should also be noted that with a slight modification the equations can be applied to the pseudo-second-order glass transition in polymers. Compared with the so-called genuine second-order transitions, the nature of the glass transition is anomalous with regard to the direction of the discontinuous jumps of various thermodynamic quantities, such as the heat capacity and isothermal compressibility, which appear in the equations for r_c and ΔG_c. The changes in C_p and β at T_g have signs opposite to the changes in these and similar quantites at the transition temperature for genuine second-order transition.[18]

In this paper a formalism is developed for the application of nucleation theory to first- and second-order phase transitions in the

Ehrenfest sense. As a result of this approach expressions for the critical nucleus size and critical energy barrier were obtained for the influence of applied pressure and stress on the transitions. There are also implications of important effects on the kinetics of first-order transitions.

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Figure Captions

Fig. 1: For a phase transition $\alpha \rightarrow \beta$ to occur G_β must be less than G_α where G is the molar Gibbs' free energy. This can be accomplished by (a) supercooling below the normal transition temperature T_t, (b) the application of an external pressure ΔP, or (c) the application of a tensile stress σ

Fig. 2: The two opposing energy terms which give rise to a critical radius r_c and a critical energy barrier ΔG_c for nucleation and growth.

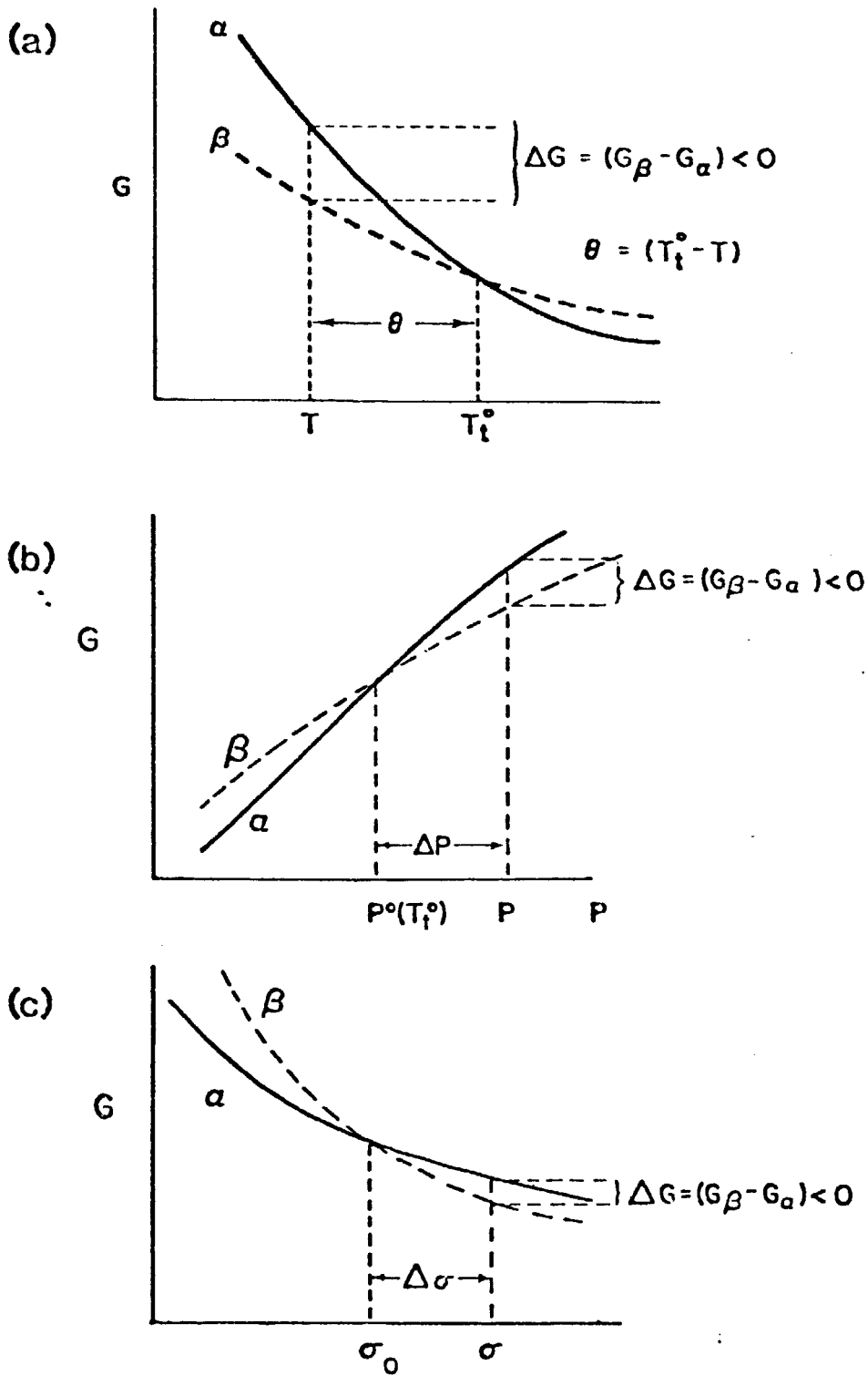

(a)
α
β
G
ΔG = (Gβ - Gα) < 0
θ = (T°t - T)
θ
T
T°t
(b)
G
ΔG = (Gβ - Gα) < 0
β
α
ΔP
P°(T°t)
P
P
(c)
β
α
G
ΔG = (Gβ - Gα) < 0
Δσ
σ0
σ

Fig. 1

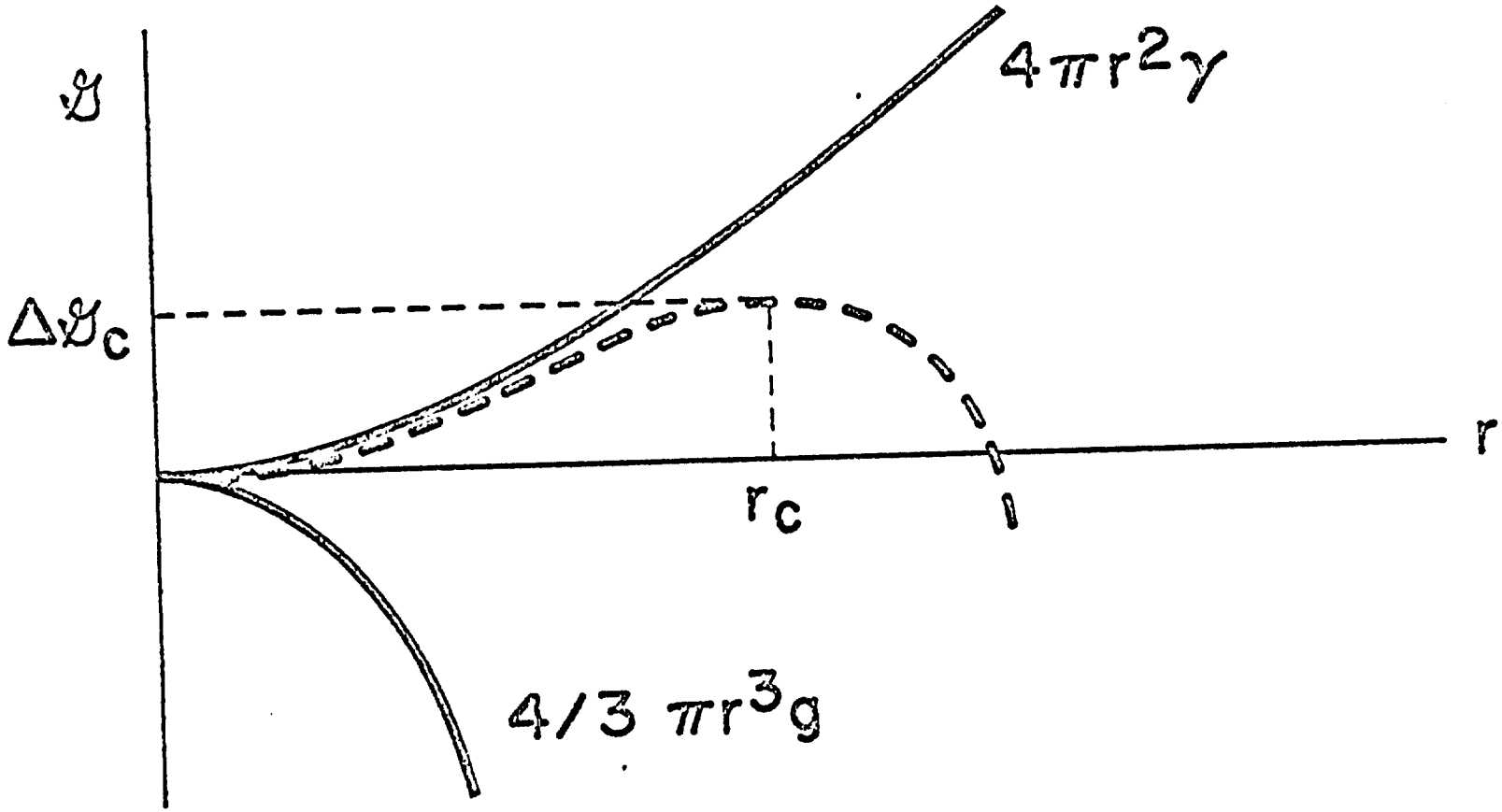


Fig. 2

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Domain Growth in Polyvinylidene Floride Considered In Terms of Ehrenfest Transitions and Nucleation Theory

R. E. BARKER, Jr.*, K. W. Campbell**, and C. C. Huang*, Department of Materials Science, University of Virginia, Charlottesville, VA. 22903.--In a previous paper [J.Appl.Phys. 56, 2386(1984)] classical nucleation theory was applied to predict the critical size r_c and energy barrier ΔG_c for Ehrenfest thermodynamic transitions ($\alpha \rightarrow \beta$) of first and second orders. The technique was to expand the excess free energy density $g = (G_\beta - G\alpha)/v_\beta$ as a Maclaurin series in the degree of undercooling $\theta = T - T_t$, and to evaluate the expansion coefficients using thermodynamic relationships. In the present paper the nucleation theory concepts are extended to the case of polarization domains in materials such as polyvinylidene flouride (PVF_2). The size $r_c = -2\gamma/g$ and barrier $\Delta G_c = (16\pi/3)\gamma^3/g^2$ are influenced the nature of the effective interfacial energy γ and by the dependence of g on the local electric field at the domain boundary. Efforts to observe macroscopic time dependent effects due to nucleation and growth phenomena are discussed.
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